PART I

THE PYROLYSIS OF VINYL ESTERS AND RELATED COMPOUNDS

PART II

STUDIES IN ONSET TEMPERATURES

APPENDIX

ATTEMPTED PREPARATIONS OF ISOTACTIC POLYMERS

by

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A Thesis submitted in accordance with the regulations governing the award of the Degree of Doctor of Philosophy in the Faculty of Science of the University of Glasgow.

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Preface

This thesis describes three research projects carried out under the direction of Professor P.D. Ritchie, B.Sc., Ph.D., F.R.I.C., F.P.I., M.I.Chem.E., F.R.S.E., in the Department of Chemical Technology, The Royal College of Science and Technology, Glasgow.

The author would like to thank Professor Ritchie for his kind help, guidance and suggestions throughout the course of this work. Also my colleagues and members of the Department Staff for their assistance and helpful discussions. The members of the Technical Workshop for the construction of apparatus.

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September, 1961.

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PART I

1. Introduction

"The transformation of a compound into another substance, or into other substances, through the agency of heat alone, is called pyrolysis" - Hurd[1].

In this jet and space age, more and more emphasis is placed on thermal stability and it has therefore become increasingly important to investigate the behaviour of various materials at elevated temperatures. Over the past few years in these laboratories, Ritchie[2,3] *et al.* have made a systematic study of the thermal decomposition of poly(ethylene fumarate) crosslinked with an unsaturated monomer and also of the degradation of the commercially important ester, poly(ethylene terephthalate) [Terylene; Dacron]. It was soon realised that the pyrolysis of these compounds led to extremely complex results owing to the diversity of the breakdown products obtained. It was decided, therefore, to concentrate on investigating the pyrolysis of various related esters and model compounds which could be regarded as representing fragments of the original polymer chain or products of the degradation of these chains. This led to results which were easier to interpret and yet gave an insight to the complex degradations of these esters. The present work continues along these lines and follows basically the principles and methods laid down by these workers[2,3].

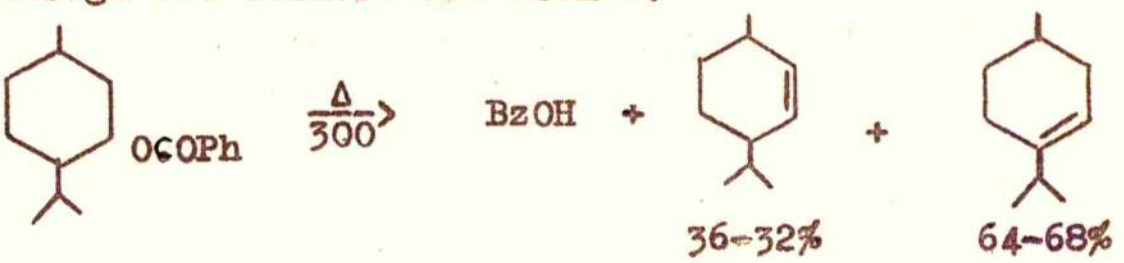
1.1. Pyrolysis of Esters

It has been known for over a century that an alkyl ester when heated at 300° - 550° decomposes into an olefin and carboxylic acid. Originally it was thought that there was one exclusive route in ester breakdown, but more recent work has shown that almost all esters break down by two or more primary competitive routes. With the advent of new and improved methods of detection, notably vapour phase chromatography, it has even been shown that one particular type of ester breakdown can yield several structurally isomeric compounds, depending on steric, thermodynamic and statistical factors in the starting and breakdown products. Thus, though Bailey[5,6] and his co-workers claimed that pyrolytic elimination of unsymmetrical secondary and tertiary acetates yielded exclusively the olefin bearing the least number of alkyl groups, it has more recently been shown[7,8,9] that all such pyrolytic acetate eliminations lead to mixtures of olefin. Thus s-butyl acetate yields 28% trans-but-2-ene, 15% cis-but-2-ene, and 57% but-1-ene according to the breakdown scheme;

$$CH_3 \cdot CH_2 \cdot \underset{\displaystyle O \cdot Ac}{\underset{|}{CH}} \cdot CH_3 \longrightarrow \underset{\text{cis and trans}}{CH_3 \cdot CH = CH \cdot CH_3} + CH_3 \cdot CH_2 \cdot CH = CH_2$$

However, the literature records several esters that break down smoothly by only one route. Barton[10] has shown that (-)-menthyl benzoate pyrolyses by only one route,

though two isomers are formed.



An interesting point is that in the absence of catalyst cyclohexyl benzoate pyrolyses as above to acid plus olefin, whereas in the presence of nickel catalyst it gives several other products, including benzaldehyde, diphenyl and cyclohexanone[11]. Another ester breaking down by a single pyrolytic route is phenyl formate,[12] which yields exclusively phenol and carbon monoxide.

Generally, however, esters tend to decompose by a number of primary competitive breakdown routes: thus alkyl acetate[13] decomposes by two primary routes, vinyl benzoate[2] by three, and phenyl α-methylacrylate[14] by four. In addition to these primary breakdown routes, secondary and even tertiary breakdown of the original primary products can occur.

Several workers have put forward tentative rules for predicting the probable routes of pyrolysis. Thus Peytral[15], and later Rice and Teller[16], put forward the Rule of Least Molecular Deformation. Briefly, this states that decomposition by heat alone will follow the reaction-route which requires the least possible deformation of the molecule. Thus, in an endothermic reaction, the atomic bonds in the resultant new compounds tend to be as nearly identical as

possible with those in the original compound. As stated more recently by Rice[16], a purely thermal reaction will be favoured when there is a maximum gain in resonance energy in the transition state and a minimum change in the electronic configuration. A typical simple reaction in accord with this is the formation of small amounts of phosgene from the pyrolysis of trichloromethyl chloroformate

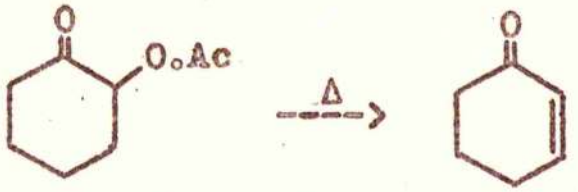
$$Cl.CO.O.CCl_3 \longrightarrow 2\ CO.Cl_2$$

Maccoll[18], in an elaboration of Rice's work, states the same view but includes in his analysis the effect of inductive forces in the stabilisation of the transition state. More recently still, DePuy[8], as a result of work on acetates, states that the transition state during a pyrolysis resembles the products more than the reactants, and that the ease of pyrolysis depends mainly on the ground state energy of the pyrolysand.

The pyrolytic breakdown of unsymmetrical secondary and tertiary acetates was stated by Bailey *et al.*[5,6] to form the olefin bearing the least number of alkyl groups, according to the Hofmann[19] rule. This, however, has recently been shown to be in error, as all pyrolytic acetate eliminations lead to mixtures of olefin, the most highly substituted olefin actually predominating in alicylic esters.[7,9,20] For non-cyclic acetates the Hofmann product predominates, but this can also be explained on grounds other than those based on the Hofmann rule. Steric and

statistical factors favour the formation of the least substituted olefin, and, therefore, other conditions being equal, the ease of hydrogen removal in acetate pyrolysis is that predicted by the Saytzeff rule (i.e. hydrogen is eliminated preferentially from the adjacent carbon atom that is poorer in hydrogen). An example of this is the pyrolysis of s-butyl acetate[8], as already mentioned, the ratio of internal : external product being 43:57. On statistical grounds alone the ratio should be 40:60.

Pyrolytic eliminations are important from both the practical and theoretical points of view. The reaction on occasion can be extremely simple in experimental procedure and, provided that the temperature of pyrolysis is not too high, the yields are normally good. For example, pyrolysis of acetoxycyclohexanone yields cyclohexenone in 96% yield[21].



Aryl acrylates and methylacrylates can also be prepared by pyrolysis of the corresponding acetoxy esters.[22]

In general, however, pyrolyses do not proceed as cleanly as the examples quoted above. The number of routes and the extent to which each occur will depend on a large number of interdependent factors, such as polarity of substituents, number of available points of scission, weak

points in the molecule, and steric, statistical, and thermodynamic effects. External conditions will also affect the final products of the pyrolysis. Thus, higher temperatures can give rise to new routes and catalysts may alter the scheme of the reaction. During the course of this work these effects have been minimised by maintaining steady temperatures during a pyrolysis, and by using either quartz or glass apparatus, the catalytic action of which seems in practice to be unimportant. Carbonisation, which accompanies most pyrolyses at higher temperatures, was believed to affect the breakdown[23], but more recent work by Bailey[24] and Royals[9] has shown that this has very little effect, either qualitatively or quantitatively.

1.2. Pyrolysis Routes

General classification

Individual types of ester pyrolysis have been classified under the following nomenclature by Ritchie.[25]

Type A - Alkyl oxygen scission

Alkyl-oxygen scission can be sub-divided into three classes, A^0, A^1 and A^2, depending on whether the alkyl portion contains no β-hydrogen, contains a β-hydrogen and is saturated, contains a β-hydrogen and is unsaturated, respectively.

A^1, the most important route in ester pyrolysis, involves the migration of a β-hydrogen atom from the alkyl

group on to the alkyl-oxygen atom.

$$R.CO_2.CH_2.CH.R_2' \longrightarrow R.CO_2H + CH_2 = CHR_2'$$

Type B - Acyl-oxygen scission

This class can be divided into two groups, B^1 and B^2, as a hydrogen atom can migrate from either of two sites, leading to two different products. In the absence of a β-hydrogen atom this is normally the predominating route, yielding either two carbonyl compounds or an alcohol and keten :

$$B^1 \quad > CH.CO \,|\, O.CH < \longrightarrow \; > C = O + HO.CH <$$

$$B^2 \quad > CH.CO \,|\, O.CH < \longrightarrow \; > CH.CHO + O : C <$$

The B^2 scission is a reversal of the Tishchenko[26] reaction, a mutual addition of two carbonyl molecules in the presence of aluminium alkoxide.

$$2\ R.COX \longrightarrow R.CO_2CRX_2$$

R = alkyl or aryl

X = H or CN

Type C - Elimination of CO or CO_2

This consists of two groups, C^1, decarbonylation, and C^2, decarboxylation. C^1 is a reaction characteristic of aldehydes and ketones rather than esters, but it is undergone by a few esters of specialised structure.

$$R.CO_2R' \longrightarrow CO + R - O - R' \text{ (or isomer)}$$

C^2 (decarboxylation), once considered unusual in ester pyrolysis is actually quite common, provided that R and/or R' are unsaturated

$$R.CO_2R' \longrightarrow CO_2 + R.R'$$

Type D - Disproportionation

This involves the breaking of an ester, usually unsymmetrical into two more symmetrical fragments.

$$R.CO_2.CH_2O_2C.R \longrightarrow R.CO.O.OC.R + CH_2O$$

Type R - Rearrangement

The ester molecule may arrange to a more stable form on pyrolysis. For example:

$$R.O_2C(CH_2)_n\ CO_2H \longrightarrow {}^1/2\ R.O_2C(CH_2)_n.CO_2R + {}^1/2\ HO_2C(CH_2)_n.CO_2H.$$

Intra-acyl scission

Here, scission occurs between the carbonyl and alkyl groups of the ester within the - CH_2:CR.CO grouping.

$$CH_2 = CH.CO_2Ph \longrightarrow CH{:}CH + H.CO_2Ph.$$ [14].

1.2.1. Detailed Discussion

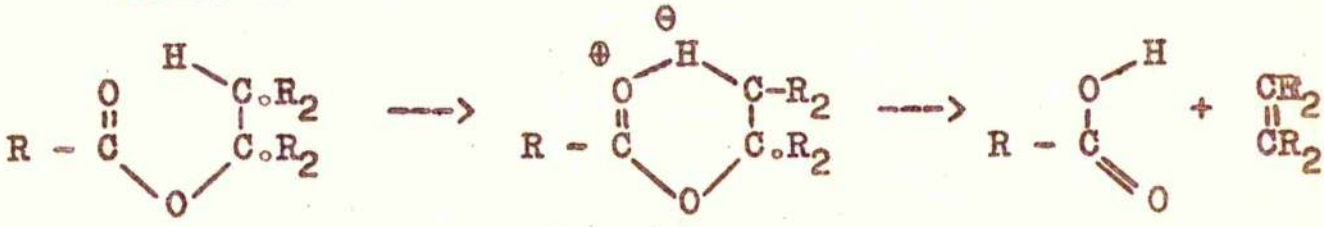
Type A^1 Alkyl-oxygen scission

A^1 scission occurs in esters with an available β-hydrogen atom on the alkyl group, taking place between the alkyl group and the ether oxygen with migration of the hydrogen atom to form the carboxyl group. The products are an acid and olefin. This reaction was first established

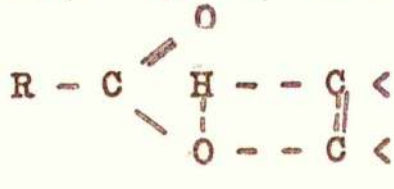
(for ethyl acetate) by Heintz[4] and later by Oppenheim and Precht[27]. The reaction was further studied by Hurd and Blunck[28] who proposed two mechanisms to account for it:

(a) a chain mechanism with univalent radicals as intermediates. This, however, they discarded, as the mechanism calls for more products than can be accounted for experimentally.

(b) a cyclic hydrogen bridge. This scheme proposed that esters undergoing pyrolysis broke down by a mechanism involving hydrogen bridges. Esters possessing a β-hydrogen atom would undergo a chelate type of 6-atom ring closure <u>via</u> a hydrogen bridge. Rearrangement of the electrons would give rise to an acid and olefin as follows:



Several other mechanisms have been advanced, notably by Bilger and Hibbert[29], who explained the reaction by a radical theory as developed and extended from Nef's[30] dissociation theory, and by Warwick and Fugassi[31] who proposed that the transition state could be regarded as a pseudo four-centre system of the form



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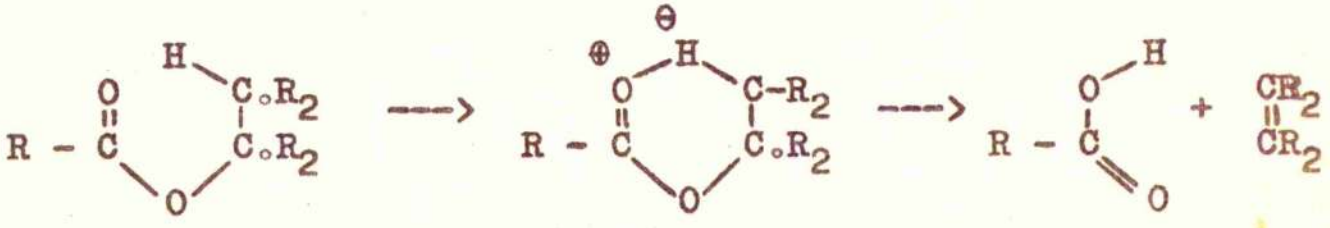

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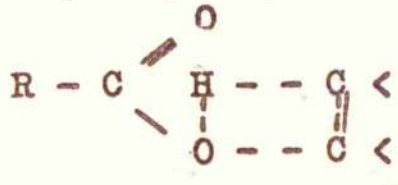


Blades[32] extended these studies using the toluene flow technique but could detect no evidence of a free radical mechanism.

However, the cyclic mechanism originally proposed by Hurd and Blunck is now fairly generally accepted; and it agrees well with the cis nature of A^1 eliminations, as discussed by Barton.[33] Recent work in these laboratories by Golomb[24] on lactones and lactides has also given further weight to Hurd's proposal.

During the course of his investigations, Hurd found that tertiary esters underwent A^1 scission in the region of 225°, whereas primary esters required much more rigorous conditions. This effect has been borne out by Maccoll[35], who found the following progressive increase in the relative rates of pyrolysis in passing from primary to tertiary alkyl formates and acetates.

	Et	Pr^i	Bu^t
Acetate	1	26	515
Formate	1	20	720

From this it can be seen that variation of the acid has only a relatively small effect on the rate, whereas the degree of substitution at the α-carbon atom of the alkyl group has a large effect.

A great deal of work has been done recently in elucidating the nature of the transition state and in predicting the direction of elimination. Thus, DePuy[21] found that for non-cyclic acetates the Hofmann product predominated,

but that as steric and statistical factors favoured its formation, the actual ease of hydrogen removal is that predicted by the Saytzeff rule. This is substantiated by Barton[10], who found that in the pyrolysis of (-)-menthyl benzoate, (+)-p -menth-2-ene and (+)-p -menth-3-ene were formed in the ratio 1:2 as would be expected if the Saytzeff rule were obeyed.

Maccoll[35] has shown that the reaction can be thought of as quasi-heterolytic, approximating the E_2 mechanism in solution. A covalent bond may be broken or formed in two different ways, heterolytic or homolytic, the latter requiring about an additional 100 k.cals. of dissociation energy. However, in a solvent of high dielectric constant, this energy relationship will be reversed, so that gas phase reactions proceeding through ion pairs are not energetically prohibited. Maccoll's evidence is based on three facts:-

(a) the relative rates of the α-methylated series

	Ethyl	Pr^i	Bu^t
Formate	1	20	720
Acetate	1	26	515
Alkylsulphonium ion (known E_2 mechanism)	1	23	586

(b) the Hofmann orientation,

(c) the inductive effect of the carbonyl group in Me.CO.O.CO.Me as compared with Me.CO.O.CH_2.Me, causing a strong inductive withdrawal of electrons from the

β-hydrogen atom, which will augment the effect of the carbonyl-oxygen atom.

He concludes that the reaction is best considered as a nucleophilic attack of the acyl-oxygen on the β-hydrogen atom, and that the forming O - H bond determines the rate, not the breaking alkyl-oxygen bond.

This also shows that branching at the α-carbon greatly accelerates the reaction, bond breaking being facilitated by hyper-conjugative effects. Stevenson[36] showed that as branching at the α-carbon is increased the activation energy for homolytic dissociation becomes similar to that for heterolytic dissociation, and that the activation process in the gas phase is heterolytic rather than homolytic.

Though Maccoll holds to the Hofmann theory, which Ingold points out as implying inductive control of the reaction, several recent papers have questioned the specificity of direction of elimination. Three or possibly four factors determine the ratios of the products formed in the pyrolysis of esters, as follows:

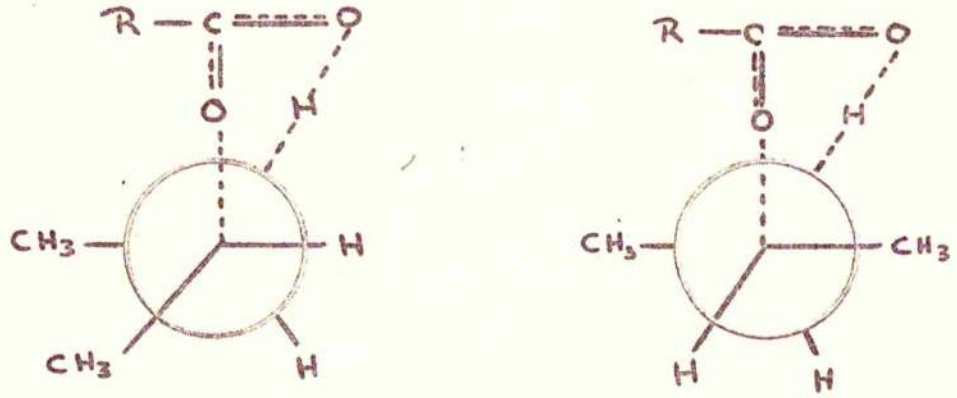
(a) The statistical effect of the number of available hydrogen atoms in the various positions.

(b) The repulsive interactions of groups in the transition state of the elimination (a steric effect).

(c) The relative thermodynamic stability of the olefinic products formed.

(d) The relative acidity of the hydrogen atom removed. This may become important, though only in esters with especially activated hydrogen atoms.

Thus, in the pyrolysis of s-butyl acetate the olefins formed were quantitatively in close agreement with the ratios expected on statistical grounds (but-1-ene: but-2-ene = 57:43). However, the trans form of but-2-ene predominated. This can be interpreted on steric grounds as due to methyl-methyl repulsion in the transition state, leading to the cis olefin, a repulsion which is absent in the transition state leading to trans olefin.



Thermodynamic effects account for the ratio being 57:43 and not 60:40 as would be expected on purely statistical accounts.

By pyrolysis of 1-methylcyclohexyl acetate and its deutero analogue, DePuy[21] showed that the C - H bond was being broken in the transition state. His results, however, do not show that simultaneous O - H bond formation is significant, as would be expected for a highly concerted cyclic mechanism. Maccoll has shown that ethyl, isopropyl and t-butyl acetates react in the order expected if heterolytic bond breaking is important, but he has pointed out that they react at much lower rates than would be expected

for a carbonium ion mechanism. DePuy and Leary[37] have also obtained results on pyrolysis of p-methoxybenzyl acetates showing inconsistencies with the development ofappreciable positive charge in the transition stage. Further, DePuy has shown that the amount of C - O heterolytic bond-breaking must be very small, which, therefore, throws some doubt on Maccoll's statement that it is primarily the forming O - H bond that determines the rate.

DePuy, Bishop and Goeders[38] have recently examined the effect on the product-distribution of increasing the strength of the acid being eliminated from various s-butyl esters.

	Temp.°	but-1-ene	trans-but-2-ene	cis-but-2-e
Acetate	450	57	28	15
Chloroacetate	375°	57	28	15
Dichloroacetate	425°	54	30	16
Trifluoroacetate	335°	52	31	17

This tends to show that A^1 reactions are not sensitive to inductive or resonance effects, as elimination by successively more polar mechanisms does not lead to an increase in the proportion of but-2-ene.

One can therefore conclude that the C— H bond is broken in the transition state, but that the acidity of the hydrogen being removed is not of primary importance. Substituents at both the α-carbon and the β-carbon atom exert an influence paralleling that which they will exert

on the olefinic product, and consequently statistical and steric effects being equal, the more stable olefin predominates among the products. It may be assumed that the transition state is best described as one in which both the C - H and C - O bonds are to a large extent broken and much double bond character has developed, but in which no appreciable charge separation is evident.

In view of the number of conflicting and contradictory reports in the current literature, no definite conclusions can be drawn and the above must be considered a tentative approach.

1.2.2. Type A^2 - Alkenyl - oxygen scission

This route may be compared to the alkyl-oxygen scission of saturated esters, and though there are very few examples in the literature, it is probable that the mechanism is similar to that suggested by Hurd and Blunck for A^1. It is of the general nature:

$$R.CO_2.CH{:}CH.R' \longrightarrow R.CO_2H + CH \equiv CR'$$

Thus, Ritchie[2] found that one of the minor products in the pyrolysis of vinyl benzoate was acetylene:

$$BzO.CH{:}CH_2 \longrightarrow BzOH + CH{:}CH$$

The reaction occurs to only a small extent, Steedman[39] reporting 2.8% of acetylene in the gaseous pyrolysate (cracking temperature 475°).

The minor nature of the reaction as compared to A^1 can perhaps be attributed to the differences in bond

dissociation energies between R.CH:CH - H and R.CH_2.CH_2 - H. Field[40] gives D(C_2H_3- H) as 122 k.cal. and Stevenson[41], using electron impact methods, has extrapolated a value of 96 k.cal for D(C_2H_5- H).

1.2.3. Type A° Alkyl - oxygen scission

This type of scission can occur when no β-hydrogen is available. Again, it occurs to only a very minor extent, the B-type reaction, which would be preferred on energetic grounds, tending to predominate.

Peytral[42] detected acetic acid in the pyrolysis of methyl acetate:

$$CH_3.CO_2.CH_3 \longrightarrow CH_3.CO_2H + {}^1/_2\ CH_2{:}CH_2$$

High temperatures are required for this reaction, and it would appear to be radical in nature. Methyl esters, quite generally, possess a comparatively high stability towards heat, and Hurd[28] suggests that this is due to their inability to form a 6-membered cyclic transition state (see Fig.3). ? See Note below pp 34-35 ?

1.2.4. Type B^1 and B^2. Acyl - oxygen scission

This scission is in contrast to alkyl-oxygen scission as it involves the transfer of an α-hydrogen atom to the carbonyl group. Migration of the hydrogen atom can occur in both directions, either from the acyl to the alkoxy group (B^1) or vice versa (B^2).

An example of B^1 scission is the pyrolysis of phenyl acetate[28], where alkyl-oxygen scission is precluded by the lack of a β-hydrogen atom:

$$CH_3.CO.O.Ph \longrightarrow Ph.OH + CH_2:CO$$

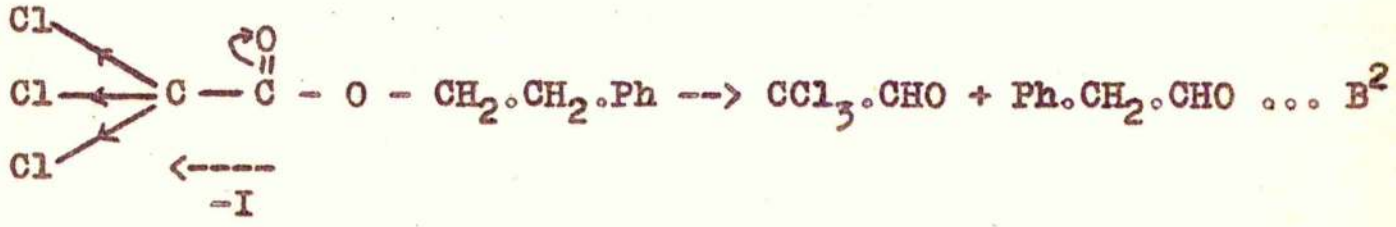
B^2 scission is the reaction favoured in esters which lack a β-hydrogen atom, the products being either two similar or dissimilar aldehydes or ketones. Even when it is possible for an A^1 scission to occur, B^2 is often a competing route. Thus the pyrolysis of ethyl succinate[43] can be shown to proceed by at least two routes:

$$Et.O_2C(CH_2)_2.CO_2Et \begin{cases} \longrightarrow HO_2C.(CH_2)_2.CO_2H + 2\ CH_2:CH_2 \ldots A^1 \\ \longrightarrow OHC.(CH_2)_2.CHO + 2\ CH_3.CHO \ldots B^2 \end{cases}$$

Where A type scissions cannot occur, the major route is normally the B^2 scission, e.g. in benzyl benzoate:[44]

$$BzO.CH_2.Ph \longrightarrow 2\ Ph.CHO.$$

An interesting example of B^2 scission exclusively, even where the A^1 route is not ruled out, is in the pyrolysis of β-phenylethyl trichloroacetate:



This is due to the polar character of the CCl_3 unit and would imply inductive control of the mechanism.

1.2.5. Type C^1. Decarbonylation

Decarbonylation of aldehydes is a well known and quite general reaction proceeding *via* a homolytic decomposition. However, there are very few instances of esters undergoing direct decarbonylation. Usually, therefore, when decarbonylation occurs in an ester, the ester itself either contains an aldehydic or ketonic carbonyl, or the decarbonylation follows as a secondary reaction, the ester first having undergone a B type scission or a rearrangement. Calvin and Lemmon[45] mention a true example of ester decarbonylation: using tracer techniques in the pyrolysis of ethyl pyruvate, they established that carbon monoxide elimination occurred from the ester grouping, not from the α-keto group:

$$CH_3{}^{14}CO.CO_2Et. \longrightarrow CO + {}^{14}C \text{ by-products.}$$

No specific mechanism has yet been put foward.

1.2.6. Type C^2. Decarboxylation

Till recently decarboxylation of esters was considered a rather unusual mode of thermal decomposition, though Auschutz[46] had observed it in the pyrolysis of phenyl maleate as early as 1885. It has now been shown that the reaction is of a far more general nature. For example, phenyl acrylate[14] yields some styrene and carbon dioxide:

$$CH_2{:}CH.CO_2Ph \xrightarrow{500^\circ} CO_2 + CH_2{:}CH.Ph.$$

The same products are given by vinyl benzoate[2], which

is isomeric with phenyl acrylate:

$$Ph.CO_2.CH{:}CH_2 \xrightarrow{500} Ph.CH{:}CH_2 + CO_2$$

A noticeable factor is that all the examples quoted in the literature display the same characteristics, namely unsaturation.

There is at present no obvious mechanism for the reaction.

1.2.7. Type D. Disproportionation

This is most commonly found in unsymmetrical esters, when the ester will disproportionate to products of greater symmetry. Thus, phenyl hydrogen sebacate[47] reacts as follows:

$$2\ Ph.O_2C(CH_2)_8.CO_2H \longrightarrow Ph.O_2C.(CH_2)_8.CO_2Ph + HO_2C(CH_2)_8.CO_2H.$$

A recent example recorded in these laboratories is the disproportionation of methylene dibenzoate:[13]

$$BzO.CH_2.OBz \longrightarrow Bz_2O + CH_2O$$

It is unlikely that any single reaction mechanism can account for these two reactions.

1.2.8. Type R. Rearrangement

Of particular relevance to this work is the thermal rearrangement of α, β-unsaturated esters to their isomeric β-diketones, a reaction which may be represented thus:

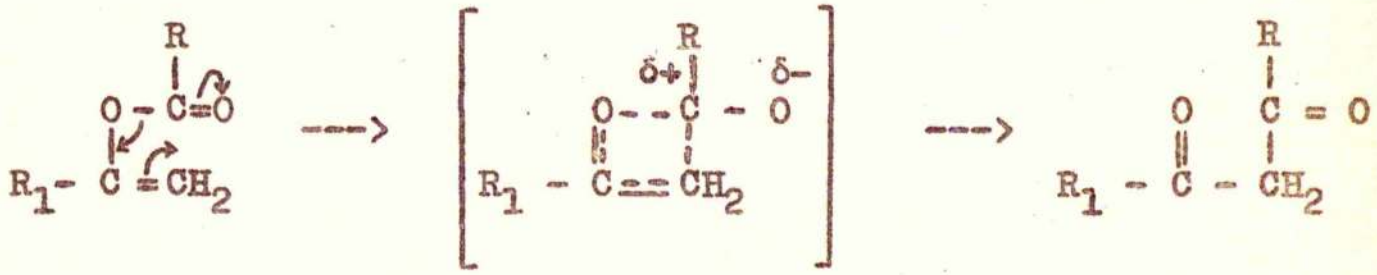
$$R.CO_2CR' {:}\ CHR'' \longrightarrow R.CO.CHR''.COR'$$

This reaction was first reported by Wislicenus[48],

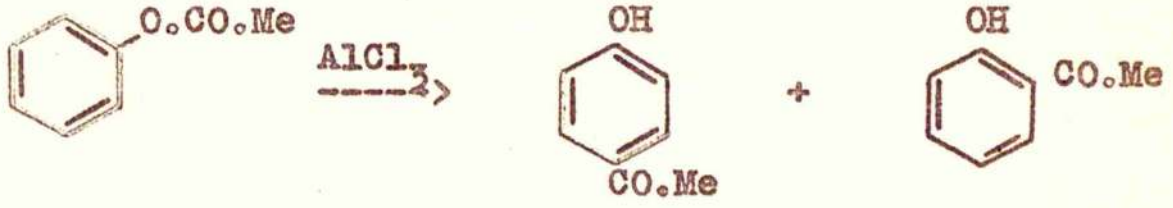
and confirmed more recently by Young.[49] An example is the conversion of the enol benzoate of acetone to benzoylacetone at 500°.

$$Ph.CO_2.CMe{:}\ CH_2 \longrightarrow Ph.CO.CH_2.CO.Me$$

Young has postulated a mechanism involving a four-membered cyclic transition state to account for the reaction.



Many types of rearrangement involving catalysts are quoted in the literature, such as the Friess rearrangement in presence of aluminium chloride:



However, a similar type of rearrangement caused by heat alone has been described by Skraup and Beng[51], though here only the o-isomer is formed.

1.3. Pyrolysis of Vinyl Benzoate

Chitwood[52], pyrolysing ethylene dibenzoate, which is a model compound for the pyrolysis of poly(ethylene terephthalate) reported that it yielded vinyl benzoate and benzoic acid by normal alkyl-oxygen scission:

$$Ph.CO_2.CH_2.CH_2.O_2C.Ph \longrightarrow Ph.CO_2.CH{:}CH_2 + Ph.CO_2H$$

Carbon monoxide was also formed. This is clearly a secondary reaction since Ritchie[2] pyrolysed vinyl benzoate and found that it broke down in the vapour phase by three competing routes as follows:

(1) A major rearrangement (R) to benzoylacetaldehyde, followed by decarbonylation (C^1) of this labile ketoaldehyde to acetophenone.

(2) Decarboxylation (C^2) to styrene.

(3) A minor alkenyl-oxygen scission (A^2) to acetylene and benzoic acid.

No trace could be found of the β-ketoaldehyde itself, this being attributed to its known instability.[53]

A number of secondary products were detected in small quantities including benzene, methane, ethylene, acetaldehyde and benzoic anhydride. Acetaldehyde and benzoic anhydride were assumed to come from the pyrolysis of ethylidene dibenzoate[14], which itself was formed from a reaction between benzoic acid and unpyrolysed starting material.

$$Ph.CO_2.CH{:}CH_2 + Ph.CO_2H \longrightarrow (Ph.CO.O)_2.CH.CH_3$$

$$\downarrow$$

$$(Ph.CO)_2O + CH_3.CHO \quad .... \quad D$$

The benzoic acid, however, as originally thought by the authors did not come exclusively from the alkenyl-oxygen scission (see later section).

It is noteworthy that no trace of any acyl-oxygen (B) scission could be detected.

2. Object of This Work

Bearing in mind the work described in Section I of this thesis, and in particular Section 1.3, it was decided to make a fuller study of the mechanism of the reactions which compete in ester pyrolysis.

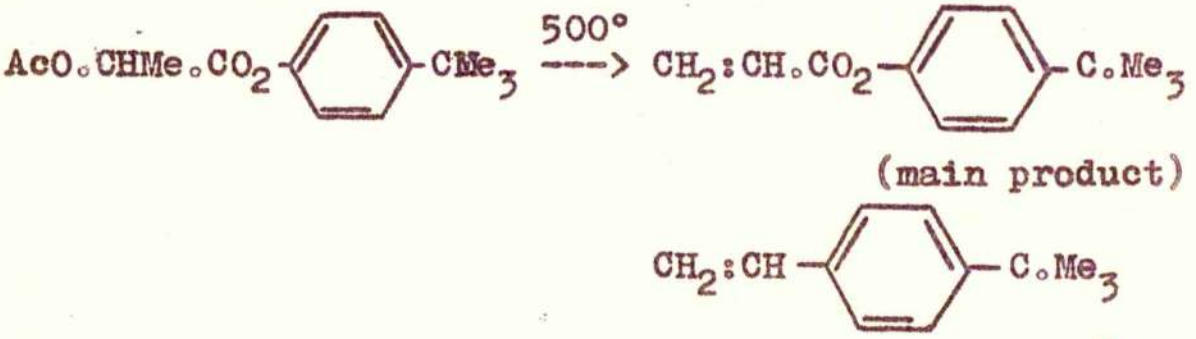
Vinyl o-, m- and p- chlorobenzoates have been prepared and pyrolysed. It was thought likely that if the decarboxylation (C^2) is free radical in type, combination of the chlorophenyl and vinyl radicals following the elimination of carbon dioxide might occur with at least a partial change in the orientation of the chloro-substituent in the resulting chlorostyrene. Similarly the rearrangement/decarbonylation (R/C^1) might yield a chloroacetophenone differing in orientation from that of the parent vinyl chlorobenzoate, though here it is more likely that the aroyl group migrates as a whole during rearrangement without detachment of the aryl group as a transient entity. In addition, the effect of the introduction of an electrophilic group into the benzene nucleus at various positions relative to the ester grouping could be studied.

2.1. Literature

No real clue to this problem is provided by the literature, though a rough parallel occurs in the work of Filachione, Lengel and Ratchford[22] on the pyrolysis of certain aryl α-acetoxypropionates. These break down mainly by the predictable A^1 scission to acetic acid and an aryl

acrylate (CH_2:CH.CO_2Ar) isomeric with the type of vinyl ester (Ar.CO_2.CH:CH_2) now under discussion.

They also found in addition, that p-t-butylphenyl α-acetoxypropionate yielded a trace of p-t-butylstyrene.



(main product)

In the light of subsequent work by Ritchie[14], this hydrocarbon must have been due to a minor decarboxylation of the aryl acrylate, which suggests that decarboxylation (of the p-isomer at least) is not accompanied by a change in orientation. However, the identification of the p-alkylstyrene was not conclusive, nor was any search for the o- and m- isomers reported: in any case, there is no reason to assume that the isomeric esters Ar.CO_2.CH:CH_2 and CH_2:CH.CO_2Ar are decarboxylated by similar mechanisms.

3. Discussion of Results

3.1. Pyrolysands

Vinyl benzoate and vinyl o-, m-, and p-chlorobenzoates were pyrolysed and their breakdown products analysed. In addition, various other compounds, occurring as products of these pyrolyses or structurally related to them, were also pyrolysed in an attempt to elucidate breakdown routes.

3.2. Qualitative and Quantitative Pyrolyses

Pyrolyses were conducted in a flow apparatus as described in Section 10.1. Where possible, all pyrolyses were carried out in the same tube and at a temperature of 500°. Qualitative estimations were made by conventional chemical techniques, infra-red spectrometry and gas-liquid and paper chromatography. Breakdown routes were estimated quantitatively by standardising the gas-liquid chromatography unit, and while the complexity of the products prevents very accurate measurement, an extremely valuable guide can be obtained.

3.3. Pyrolysis of vinyl o-, m-, and p-chlorobenzoate

Examination of the pyrolysates showed that each chloro-ester yielded a chloroacetophenone having the same isomeric orientation as the parent ester with no sign of positional isomers.

However, certain changes in orientation were noted in the decarboxylation (C^2). The o- ester gave only

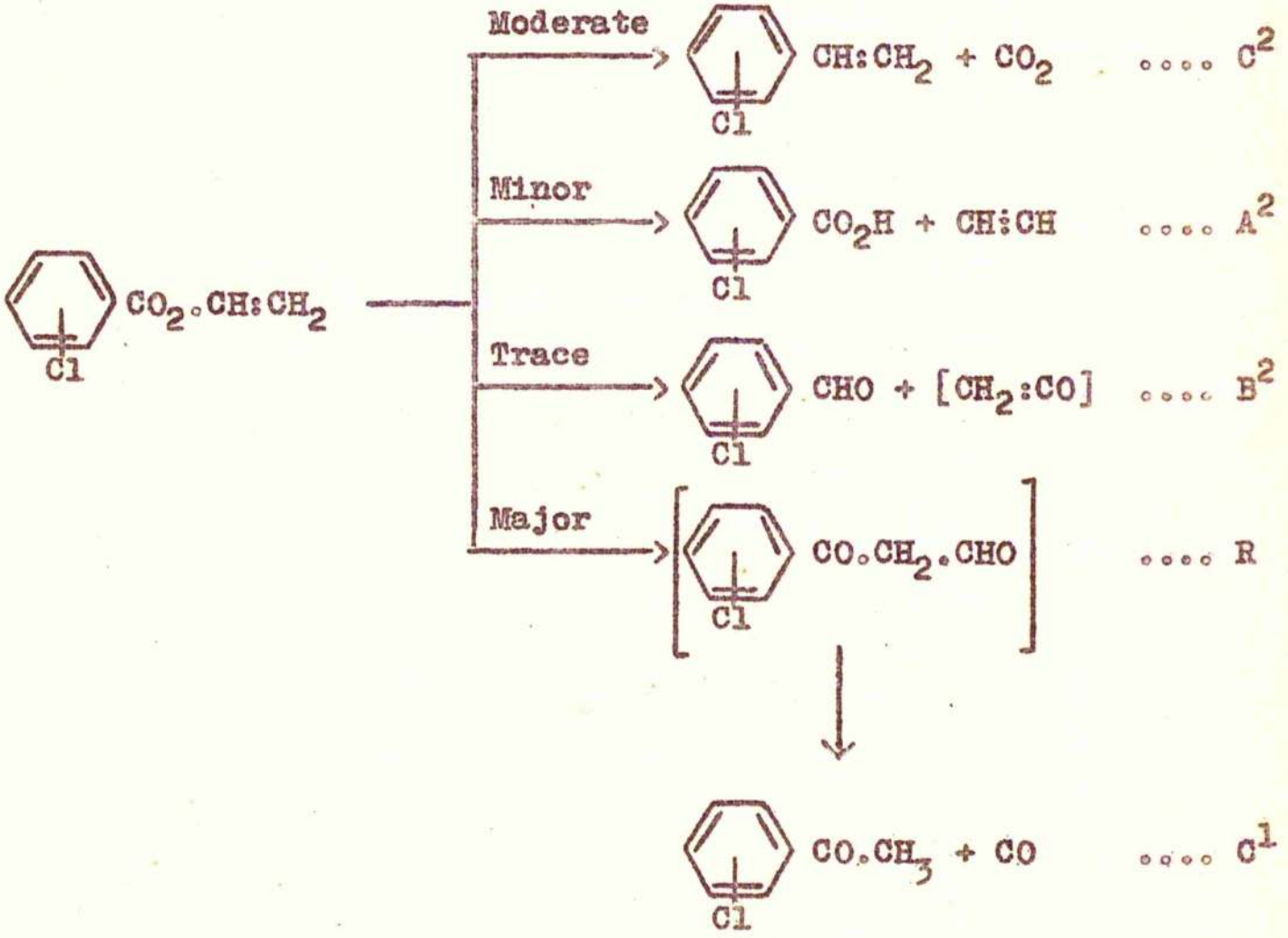
o-chlorostyrene, with no trace of the structural isomers, but the m- ester yielded mainly m-chlorostyrene with a minute trace of o-chlorostyrene and a trace of the p-isomer, while the p- ester yielded mainly p-chlorostyrene with a minute trace of o-chlorostyrene and no m-isomer.

A^2 scission, yielding the corresponding benzoic acid and acetylene, was noted as in the case of vinyl benzoate itself. However, the relatively large quantity of acid obtained could not be attributed to this route alone and some other source must be sought. This is discussed later.

The above three routes occur for vinyl benzoate[2] itself but a fourth route not observed for vinyl benzoate despite a repetition of the earlier work under more critical conditions, was also detected for the chlorobenzoates. This new route is a minor B^2 scission, yielding the corresponding chlorobenzaldehyde without change of orientation. Although this aldehyde should formally be accompanied by keten, none could be detected though carefully sought. In an effort to explain its absence, keten (prepared by pyrolysis of acetic anhydride) was dissolved in benzene and the mixture pyrolysed under the same conditions as the esters. It was found that 74% of the keten was destroyed, a figure agreeing well with that found under similar conditions by Young.[54] As the quantity of keten expected is in any case small, this secondary breakdown could explain the failure to detect it.

It is, of course, also possible that the chlorobenzaldehydes now observed occur by some minor side reaction (possibly free radical in character) other than by a B^2 mechanism, and that no keten is in fact produced.

The following overall qualitative breakdown scheme is advanced for the three chloroesters.



Other minor components of the pyrolysate, explicable as secondary products, were the chlorotoluenes, chlorobenzene, benzoic anhydrides, acetaldehyde and water.

The quantitative composition of the pyrolysate from each chloro-ester and from vinyl benzoate itself (pyrolysed under the same conditions) is summarised in Tables 1 and 2 below.

TABLE 1

Composition (wt.%) of Non-gaseous Pyrolysate from

$X - C_6H_4 \cdot CO_2 \cdot CH = CH_2$

Substituent X =	o-Cl	m-Cl	p-Cl	H
X-Acetophenone	59	55	58	54
X-Styrene	11	4	3	4
X-Benzene	2	9	2	11
X-Benzaldehyde	4	2	1	0
X-Benzoic Acid	22	28	35	18
X-Anhydride	trace	trace	trace	7
Unidentified	2	2	1	0

TABLE 2

Composition (vol.%) of Gaseous Pyrolysate from

$X - C_6H_4 \cdot CO_2 \cdot CH = CH_2$

Substituent X =	o-Cl	m-Cl	p-Cl	H
CO_2	17.5	9.0	13.0	14.0
Acetylene	3.5	7.0	5.5	3.0
Other unsat. hydrocarbons	3.0	2.5	2.0	3.0
CO	76.0	81.5	79.5	80.0
Combustibles ($<CH_4$)	trace	trace	trace	trace

3.4.1. The acyl-oxygen scission

The relative percentages of each of the isomers breaking down by a B^2 scission to the corresponding aldehyde was as follows:

TABLE 3

X =	o-Cl	m-Cl	p-Cl	H
$X.C_6H_4.CHO$ (% formed)	4	2	1	0

In vinyl benzoate and the related chloro-esters, the B^1 type scission is precluded by the absence of a α-hydrogen atom on the benzene ring, leaving B^2 scission as the only possibility.

B^2 scission, however, does not occur in vinyl benzoate: in the chloro-esters it occurs in the proportions shown in Table 3. From these figures it thus appears that the proximity of the chlorine atom to the breaking acyl-oxygen bond has an effect on the breakdown and to a certain extent regulates it.

Using Ingold's notation, chlorine has a - I and + T effect, and therefore provides one of the few cases where Holleman's rule[55] is broken, by associating o-p. orientation with deactivation. The inductive mechanism (- I) represents a permanent state of polarisation of the molecule, the conjugative mechanism (+ T) having its main effect in a

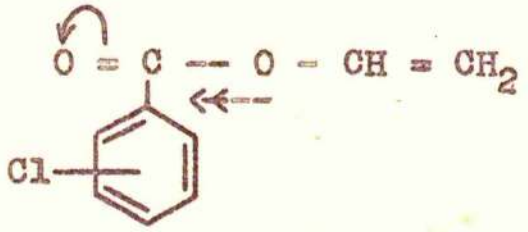
temporary process (+ E) which arises when the attacking reagent takes advantage of the polarisibility of the molecule. The electron displacements by the + T mechanism are essentially electromeric displacements + E, stimulated by the electrophilic reagent, and therefore only become important when the reagent is already at an o- or p- position and is therefore committed to an o- or p- attack. In this case, the ± T mechanism does not come into consideration: the important factor is the relative ease of breaking the acyl-oxygen bond and this is controlled by the ± I inductive effect.

In the gas phase, as distinct from the dissolved state, the reacting molecule must depend on its own resources. There can be no question, at least at the pressure used (atmospheric) of co-operative effects from other molecules. It is therefore in this sphere that the role of the substituent is most marked.

In vinyl benzoate itself it would appear that the electron attraction of the carbonyl group, the nucleophilic character of the phenyl group, and the electron repulsion of the vinyl group counterbalance one another, the result being that there is no electron displacement along the acyl-oxygen bond. This would reduce any tendency towards heterolytic fission across the bond and any fission occurring by a B^2 break would of necessity be radical. As the bond energy D(C - O) is 88 k.cal., scission would

tend to occur at other sites requiring lower energy inputs.

However, with the introduction of the electrophilic chlorine atom into the benzene ring, a strong - I effect is set up. This is about the same strength as the electron attraction of the carbonyl oxygen. However, the two forces acting together will tend to withdraw electrons from the acyl-oxygen bond towards the carbonyl carbon and into the ring. There will thus be a displacement of electrons along the C - O bond, and any tendency towards heterolytic fission will be enhanced. This can be represented as:



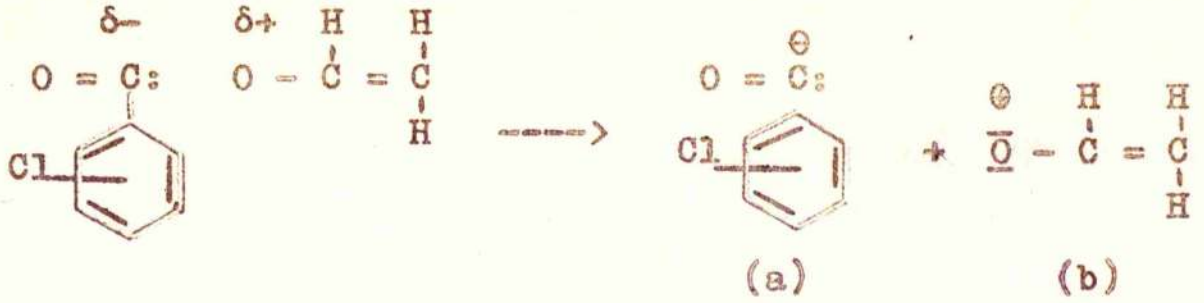
⟵ = overall effect

Because of the electronegativity of the chlorine atom, and the resulting electrical disymmetry in the C-Cl bond, there will be a concentration of electrons from the C-C and C-O bonds in the general direction of the chlorine atom. This effect is supplemented by the withdrawal of electrons from the C-O bond by the carbonyl oxygen. This particular shift (due to C = O) is present in all three isomers to the same extent: but the electron shift due to the chlorine atom will occur to varying extents, according to the relative position of the chlorine atom in the ring, i.e. its distance from the acyl-oxygen bond.

The electron displacements throughout the benzene ring are not all equal, the C-Cl dipole inducing a smaller dipole

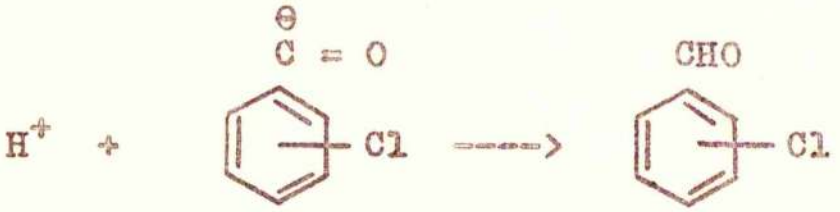
in the adjacent C-C bond because the electrons there are otherwise restrained: this in turn will induce a still smaller dipole in the next C-C bond, and so on. Thus the effect will decrease with distance from the source of the disturbance. It can be seen, therefore, that the closer the chlorine atom is to the carbonyl group (and hence the acyl-oxygen bond) the greater will be the electron dissymmetry caused in the C-O bond. This effect will then obviously facilitate a heterolytic fission: in theory the effect should decrease in order from the o-isomer, through the m- to the p-. This has undeed been borne out by experiment (see Table 3) and therefore the following mechanism is postulated for the acyl-oxygen scission in the vinyl chlorobenzoate.-

As the dielectric constant of the vapour in which the breakdown is occurring will far exceed unity owing to the relatively high dipole moments of the constituents, the reaction proceeding through ion pairs is not energetically prohibited, i.e. the "solvent" will facilitate the separation of the positive and negative ions.



(a) (b)

The carbanion (a) will be stabilised by resonance. The ion (b) will immediately lose a proton and, because of the proximity effect, this may attach itself to the newly formed carbanion. Otherwise, the carbanion may abstract a proton from some other source (see later work: pyrolysis of stilbene)



From the results obtained, it is therefore considered that the B^2 scission is ionic in nature. This fits in well with the inductive control of the reaction shown in Section 1.2.4.

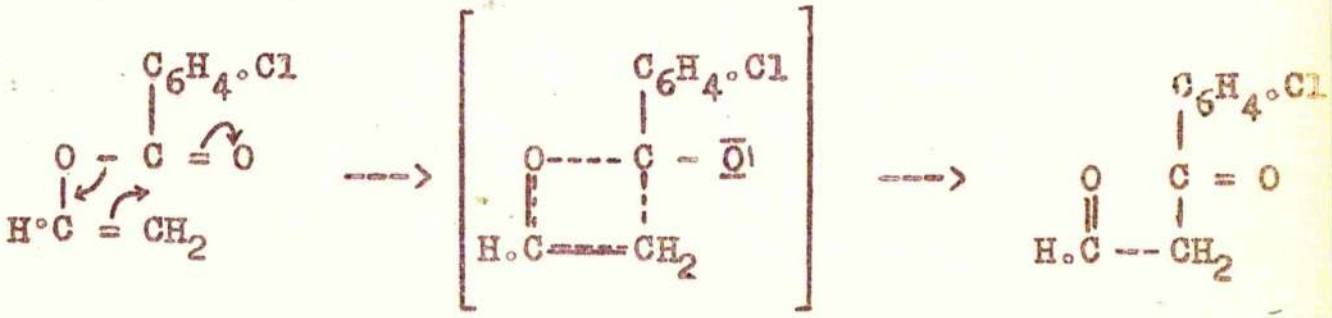
3.4.2. Rearrangement/Decarbonylation

From the figures given below it would appear that the presence or position of a chlorine atom has little or no effect on the breakdown route.

X =	o-Cl	m-Cl	p-Cl	H
X - $C_6H_4CO.Me$ (% formed)	59	55	58	54

The reaction probably proceeds through an intramolecular rearrangement (R) to the corresponding benzoylacetaldehyde followed by decarbonylation (C^1) to the chloroacetophenone.

The intramolecular mechanism proposed by Young[49] for the thermal rearrangement of enol carboxylates *via* a cyclic transition state can be applied to the vinyl chlorobenzoates in exactly the same way, thus:



No direct evidence was obtained for the presence of the labile ketoaldehyde. Ritchie[2] has pyrolysed benzoylacetaldehyde and has found the products to be carbon monoxide, acetophenone and a trace of carbon dioxide. It is assumed here that the chlorinated benzoylacetaldehydes would pyrolyse by similar routes, the overall decarbonylation being as follows:

Steedman[39] has stated that in the pyrolysis of vinyl benzoate, free radical processes play no appreciable part in the reaction scheme. The reaction must therefore be considered molecular: there is no evidence, however, that the inductive effect of the chlorine plays any large part in

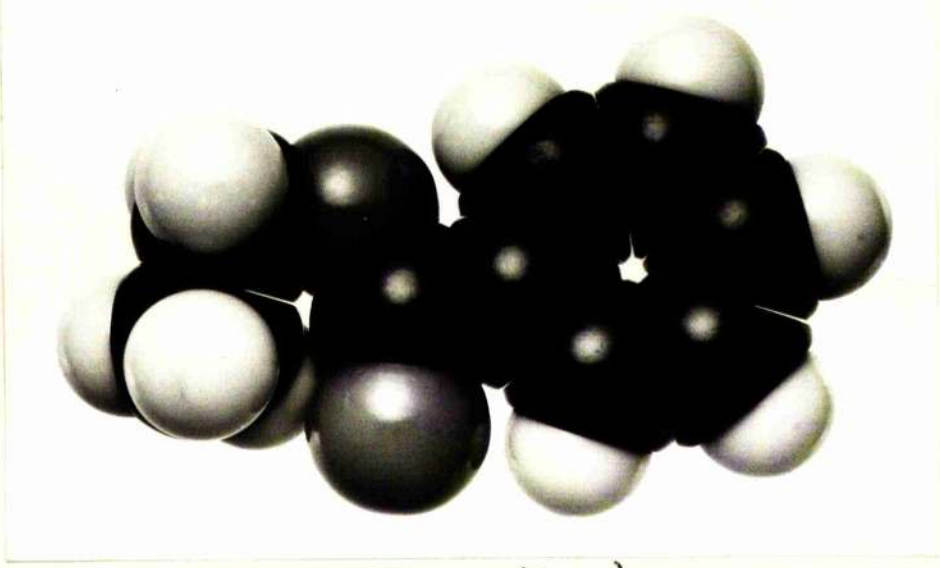


FIG. 1 (h35)

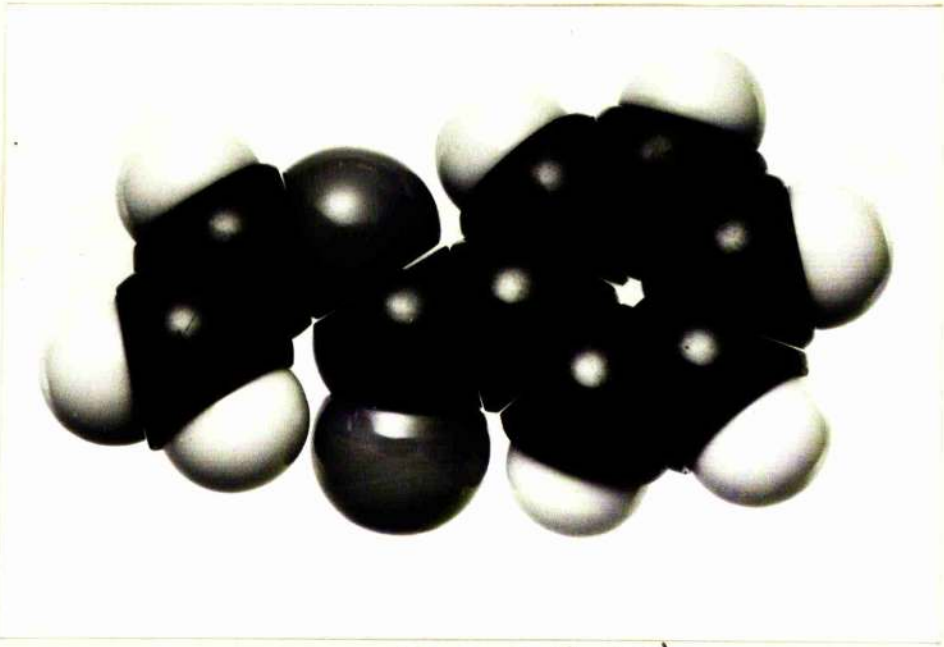


FIG. 2 (h35)

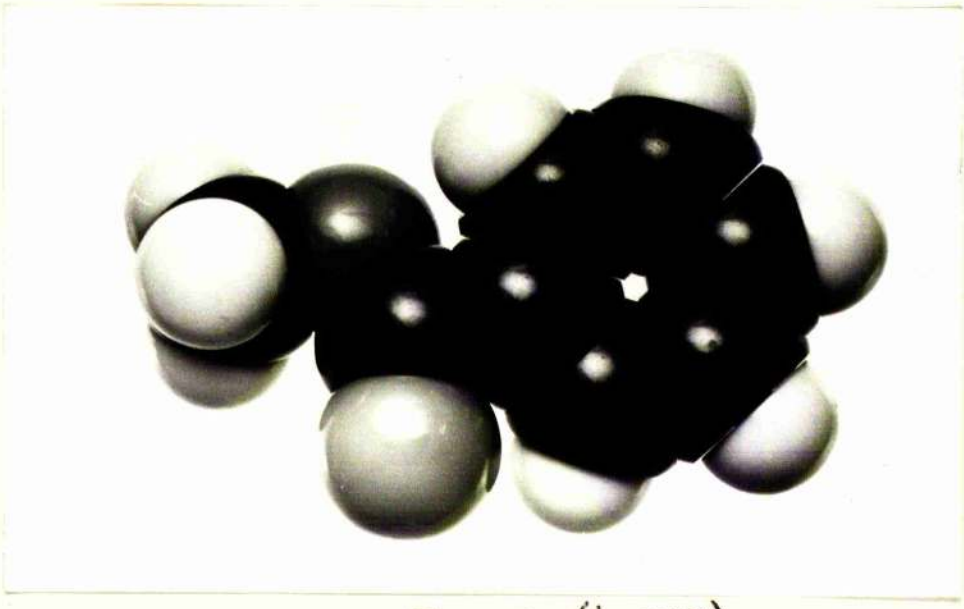


FIG. 3 (h 132)

controlling the rate of pyrolysis. This may be explained as a distance effect.

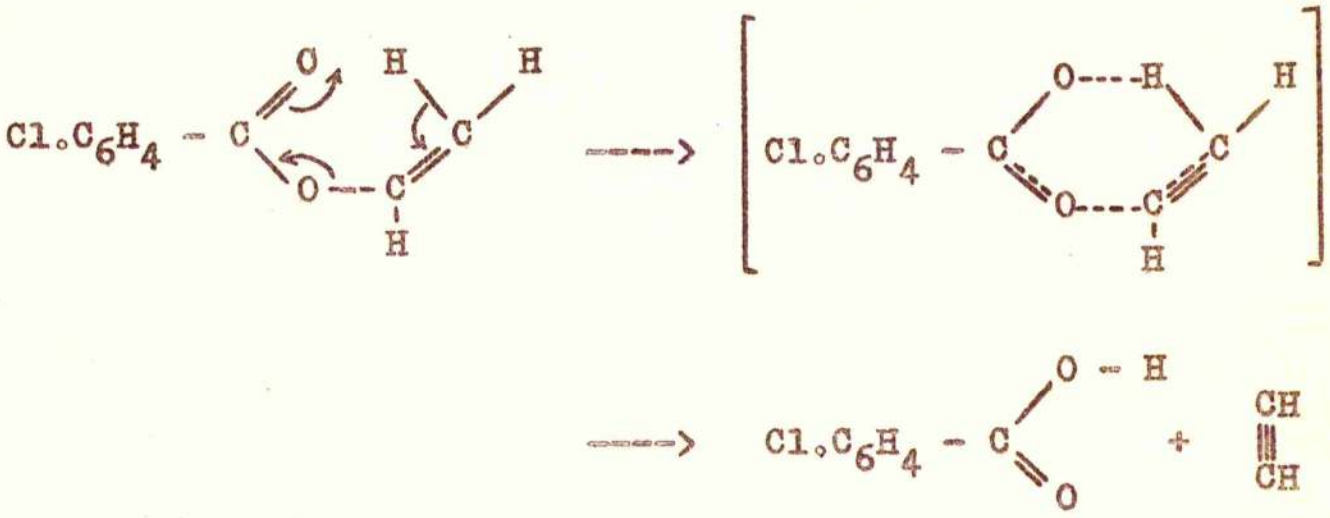
3.4.3. Alkenyl-oxygen scission

The six-membered transition stage for saturated alkyl esters has been postulated by Hurd and Blunck[28] (see Fig.1). As a development of this theory, it is now postulated that A^2, alkenyl-oxygen scission, takes place by an analogous mechanism (see Fig.2). Ritchie[56] has found that cyclohex-1-enyl esters pyrolyse by an A^2 scission though they could not identify the alkyne (known to be unstable).

Phenyl esters cannot pyrolyse in a similar manner to the cyclohex-1-enyl esters shown above, due to the fact that resonance occurs in the benzene ring.

The A^2 scission in each case yielded the corresponding acid and acetylene. No change in orientation would be expected since the bond between the benzene nucleus and the carbonyl carbon would not be broken if the acid was

formed via the six-membered intermediate ring postulated above. This can be represented as:



Since the chlorobenzoic acids are formed by more than one route (see Section 4), the weights of acetylene obtained on pyrolysis can be taken as a measure of the amount of ester undergoing scission by A^2.

TABLE 5

X =	o-Cl	m-Cl	p-Cl	H
Acetylene (moles) formed from 1 mol. $X.C_6H_4.CO_2.CH:CH_2$	0.0042	0.0084	0.0063	0.0035

Smith and Wetzel[57] have shown that in A^1 scission, the ease of pyrolysis of an ester is directly proportional to the strength of the acid to which it is related. This is in contrast to the work of DePuy[38], who claims that acid strength has no effect on product distribution. However, the present results seem to be more in line with those of Smith and Wetzel.

It is possible that the same forces which induce breakage of the O-H bond in strong acids may be responsible for the facile cleavage of the O-R bond in esters during pyrolysis, and, if this is so, it explains the greater ease of pyrolysis of esters of strong acids. Nevertheless, since the ionisation of acids takes place under entirely different conditions, the correlation into vapour-phase results can at best be only qualitative.

Smith and Wetzel[57] found, however, that esters of mono-o-substituted acids showed deviations from such linear relationships, particularly the o-halogenated esters. They found that there was little doubt that the o-chloro group stabilised the ester towards pyrolysis in alkyl-oxygen scission. According to this scheme, therefore, vinyl o-chlorobenzoate should be the most stable isomer. Table 6 shows the ionisation constants of the acids, $X.C_6H_4.CO_2H$.

TABLE 6

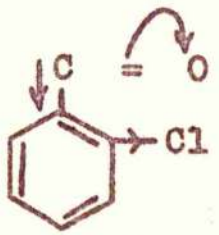
Ionisation constant	($k_a \times 10^4$)
x = o-Cl	11.97
m-Cl	1.51
p-Cl	1.04
H	0.63

From Table 5, it can be seen, that, of the three chloroesters the o-isomer undergoes least A^2 scission and the m-isomer most. This fully agrees with the work of

Smith and Wetzel, the m-acid being stronger than the p- which in turn is stronger than the unhalogenated acid.

As the o-substituents increase the dissociation of the acids, they could also weaken the O-R bonds in esters and permit them to pyrolyse more readily than esters from weaker acids. Since they do not, however, it appears that o-substitution has some other influence which retards pyrolysis by this mechanism.

The influence of the o-chlorine atom may be to cause depolarisation of the carbonyl group, thus decreasing the attraction of a β-hydrogen atom to the carbonyl oxygen.



——> electron pull

In the postulated six-membered ring intermediate, the o-chlorine may thus retard the formation of such an O-H bond, thereby stabilising the ester by preventing the formation of this cyclic transition stage.

The present results are more in line with those of Maccoll[35] than those of DePuy et al. The fact that the o-isomer produces least acetylene tends to bear out Maccoll's contention that the transition state is essentially characterised by a forming bond. Therefore, if the ring formation is more or less polar in character, the reaction can be regarded as essentially heterolytic. However, the figures obtained for the m- and p-isomers appear to be in

the wrong order. The reaction scheme is further discussed in Section 4.

3.4.4. Decarboxylation

The quantities of the three chlorostyrenes and styrene (from vinyl benzoate) are as shown below.

TABLE 7

X =	o-Cl	m-Cl	p-Cl	H
$X.C_6H_4.CH:CH_2$ formed (%)	11	4	3	4

The following changes in orientation were noted in the decarboxylation (C^2) products.

Vinyl o-chlorobenzoate ----> o-chlorostyrene (only)

" m- " ----> m-chlorostyrene (mainly)
+ o-chlorostyrene (minor)
+ p-chlorostyrene (trace)

" p- " ----> p-chlorostyrene (mainly)
+ o-chlorostyrene (trace)

The important point here is that each substituted vinyl ester yields as its main decarboxylation product a substituted styrene having the same orientation. This could be brought about by one of two reaction mechanisms:-

(a) an ionic mechanism in which the electrical charge is retained in the same position as the site vacated by the outgoing ion,

(b) an intramolecular mechanism.

The lesser products may be explained by very minor radical reactions that follow orientation rules similar to those found for radical reactions in solution. This will be discussed later.

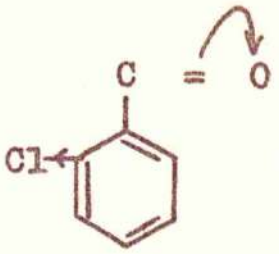
A pure gas-phase radical reaction can be ruled out, since it should produce more substances than were found experimentally. This is true in particular of the o-isomer, where no change of orientation whatsoever could be detected. Steedman[39], using inhibition techniques, has also stated that there is no evidence of any radical reaction.

A reaction of the type found in normal electrophilic aromatic substitution can also be ruled out. The - I, + T effect of the chlorine in the benzene nucleus  would come into play when the molecule was under attack from an electrophilic reagent, resulting in o-, p- substitution. Thus, any product would be a mixture of o- and p- isomers, with only a small amount of m-isomer, which is obviously not so.

This then leaves the two alternatives outlined above. Firstly consider (a).

If the reaction proceeded by an ionic mechanism, it would require scission of the C-C bond between the phenyl group and the carbonyl carbon. Here, however, (cf. B^2 scission), the inductive effect of the chlorine and oxygen (almost identical) would be working in opposite directions, thus tending to nullify each other. This would cause no material change in the electron symmetry across the bond.

It can be shown as:



Consequently this mechanism would not favour heterolytic scission.

Since the effects occur in opposite directions, it might have been predicted that the molar yields of chlorostyrenes would have been less than that of chloroaldehydes where the inductive effects are working in the same direction. In addition, the energy required to split the bonds favours the formation of the aldehydes, D(C-O) = 88 k.cal. and D(C-C) = 110 k.cal.[58] This was not found.

If the reactions were ionic, the percentage of each isomer formed would be in the reverse order to those found. It would be expected that the p- ester would yield most chlorostyrene, since, because of the distance effect of the chlorine atom, the electron dissymmetry across the C-C bond would here be a maximum. Again, this was not borne out by experiment.

There is some analogy with C-C bond breakage [Ph÷C] in the work of Rylander and Meyerson[59] who, using D-labelled toluene, showed that phenyl ions $C_6H_5^+$ are not produced by simple cleavage of the phenyl and methyl groups.

It is hence thought likely that decarboxylation proceeds <u>via</u> an ionic mechanism.

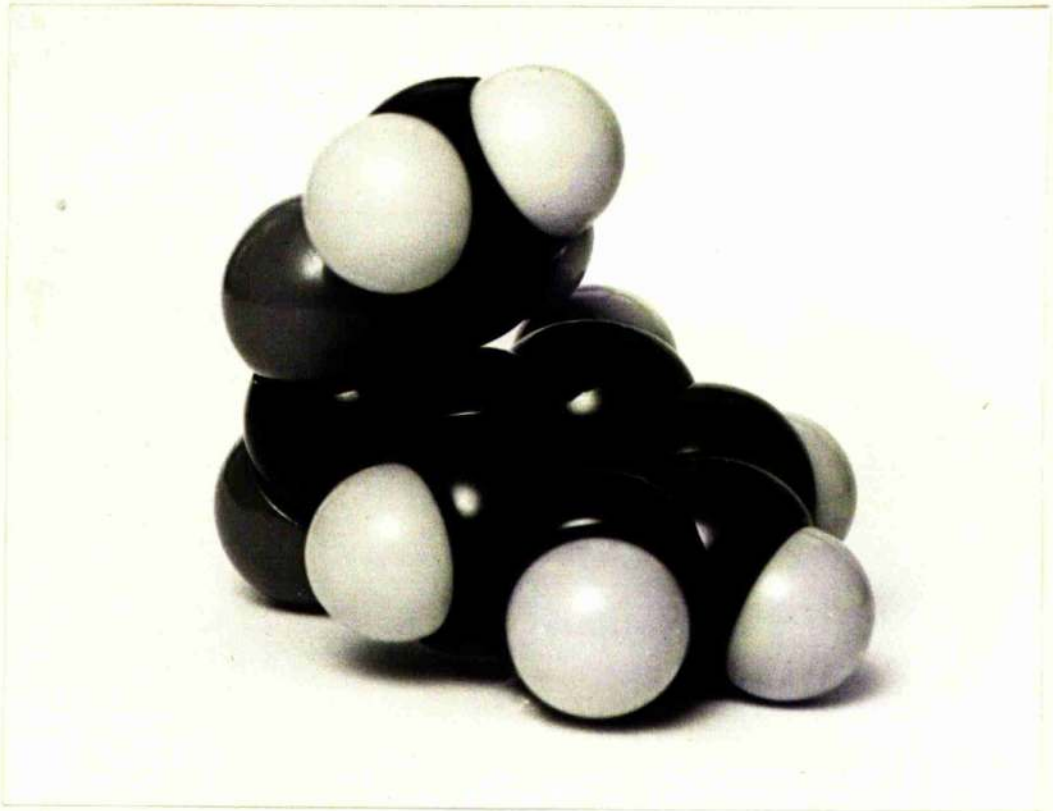
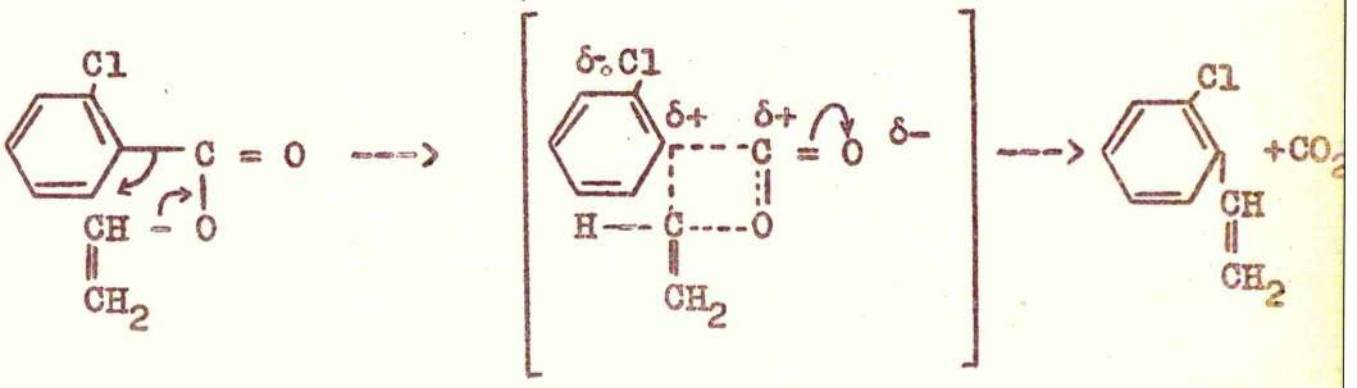


FIG. 4

Consider now alternative (b).

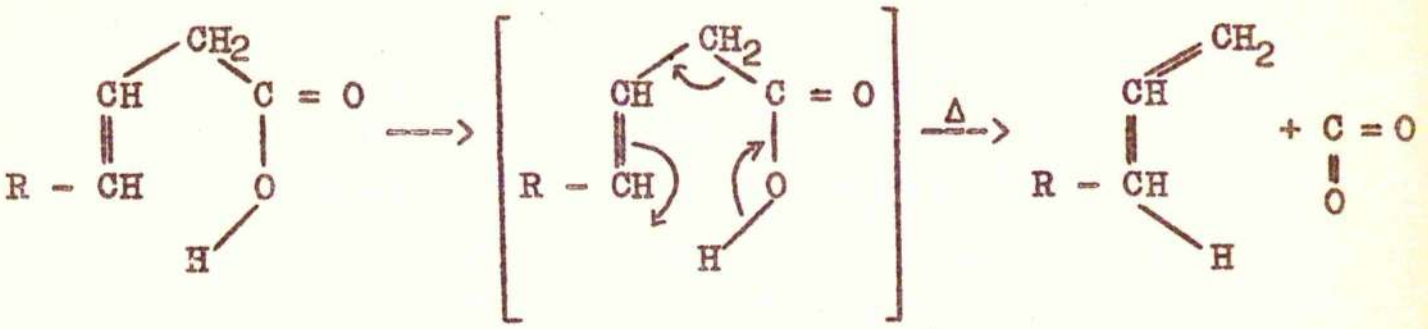
Because all the main products have the same orientation as their parent ester, an intramolecular mechanism is suggested. This involves the formation of a four-membered cyclic transition stage. (Fig 4) The reaction can be represented thus:



It is obvious from this that the original orientation of the ester would be preserved. The proximity of the chlorine to the carbon atom involved in the ring closure could account for the greater quantity of chlorostyrene formed from the o-ester, because the inductive effect of the chlorine would counteract the electron-withdrawing power of the oxygen and thus facilitate formation of the bond linking the vinyl group to the benzene nucleus.

This scheme is somewhat similar to that suggested by Arnold and Danzig[60] for the thermal decarboxylation of unsaturated acids. They state that, as a preliminary step, many α - β unsaturated acids undergo rearrangement to the β - γ form. The latter isomer is more unstable thermally, and its decarboxylation may perhaps occur via a cyclic

six-membered transition state, thus:



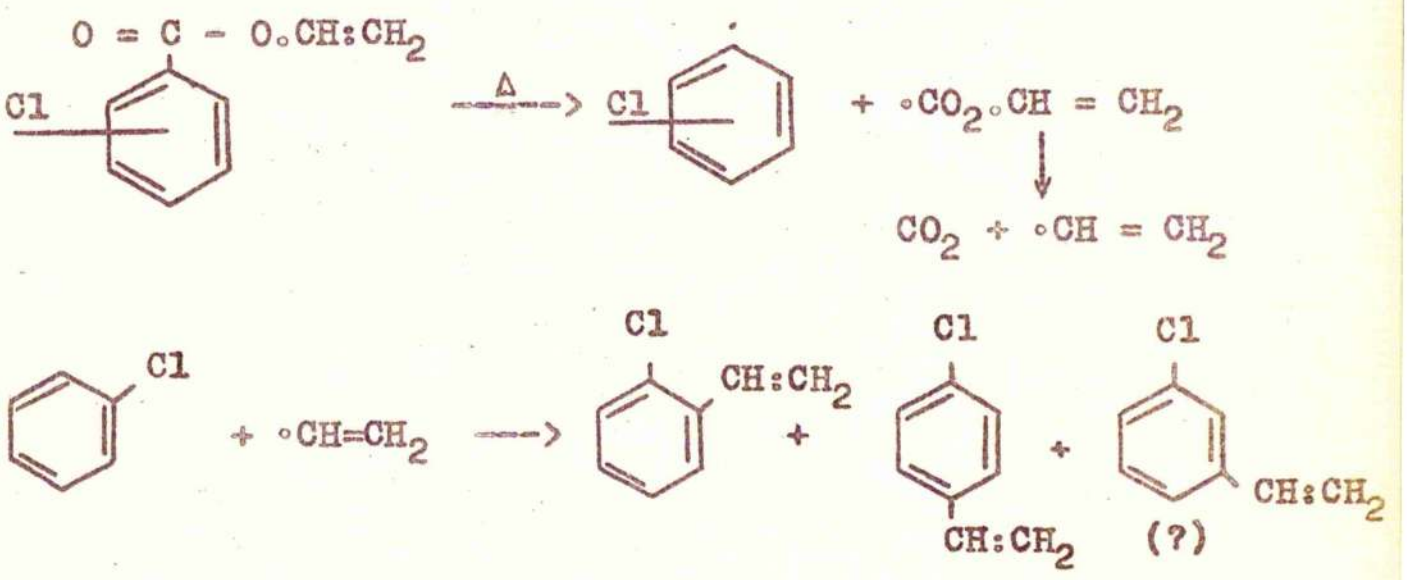
The pyrolytic formation of small quantities of other isomers differing in orientation from the parent ester can be explained by assuming a minor reaction, radical in nature occurring side by side with the ionic reaction. As Maccoll[35] has stated, it is sometimes useful to consider pyrolytic reactions as if they occurred in solution. Using this approach, it is possible to relate the work of Hey[61] and Danby[62] to the pyrolysis under consideration. These authors have determined the orientating effects of substituents in a benzene nucleus when that substituted nucleus reacts with phenyl radicals. The figures quoted for chlorobenzene are as below.

	% o-	% m-	% p-
chlorobenzene	64	23	13

Chlorobenzene is present in the system from the secondary decarboxylation of the chlorobenzoic acids.

Vinyl p-chlorobenzoate yields small quantities of o-chlorostyrene: however, no m-isomer could be detected, perhaps because of the minute quantity formed. This would be in accord with the figures quoted above.

Vinyl m-chlorobenzoate gives a small quantity of o-chlorostyrene and a trace of the p-isomer. This also agrees with the figures above. It is therefore suggested that this decarboxylation is radical in nature: as the quantities are so minute it is possible that other compounds such as diphenyl which would be expected to accompany the reaction, could not be detected. Thus:



3.4.5. Secondary Routes

A number of products which could not be accounted for by any primary routes of degradation were detected in small amounts in the pyrolysate. They included chlorobenzene, methane, ethylene, acetaldehyde and water as well as chlorotoluenes and chlorobenzoic anhydrides of undefined orientation.

Chlorobenzene will arise from decarboxylation of the corresponding benzoic acids. Methane and carbon monoxide are decomposition products of acetaldehyde, this being formed by interaction of the chlorobenzoic acid and unchanged

ester, on the lines previously established[13] for vinyl esters in general, thus:

$$Cl.C_6H_4.CO_2H + Cl.C_6H_4.CO_2CH{:}CH_2 \rightarrow Cl.C_6H_4.CO_2.CH.Me.CO_2C_6H_4.Cl$$

$$\downarrow$$

$$(Cl.C_6H_4.CO)_2O + CH_3.CHO$$

The chlorotoluenes are formed by the pyrolysis of the chloroacetophenones (see Section 6.). Toluene, previously undetected, was noted in the pyrolysate from vinyl benzoate.

Water is probably formed by the intermolecular dehydration of chlorobenzoic acids (cf. Davidson and Newman[63]), thus:

$$2\ Cl.C_6H_4.COOH \longrightarrow (Cl.C_6H_4CO)_2O + H_2O$$

The origin of the ethylene is uncertain: it is possible, however, that a vinyl radical abstracts a proton from some source (possibly the tarry by-products) thus:

$$CH_2{:}CH. + H. \longrightarrow CH_2{:}CH_2$$

4. Low Temperature Static Pyrolysis

4.1. Vinyl o-chlorobenzoate

A small sample (1.0g) of vinyl o-chlorobenzoate was heated to 250° in a static system and maintained at that temperature for twenty minutes. [For description of apparatus and technique see Part II, Section 15.1]. A bright red colouration developed. During the run, the apparatus was continuously flushed with nitrogen and the gases evolved were passed through a detection system. Acetaldehyde was the only gas produced. Allan[64] has shown that vinyl benzoate, gently refluxed with benzoic acid, yields benzoic anhydride and acetaldehyde almost quantitatively. Vinyl o-chlorobenzoate and chlorobenzoic acid should behave similarly.

In the pyrolysis of the o-ester mentioned above, it is noteworthy that no trace of acetylene could be found. Hence, although acetaldehyde was produced, presumably by way of chlorobenzoic acid (cf. Allan[64]), some mode of formation of acid other than A^2 scission must be sought.

4.2. Experimental

The pyrolysate was fractionated to give unchanged ester and a deep red residue: the latter was then subjected to numerous tests, chemical and physical.

Infra-red examination

The infra-red spectrum of the coloured compound showed marked absorption in the region 2000-2250 cm^{-1}, strongly

indicative of acetylenic linkages. This is supported by a peak at 3300 cm^{-1} normally associated with the C-H stretching vibration in RC ≡ CH. The peak at 2240 cm^{-1} confirms this terminal position: the peak at 2240 cm^{-1} is indicative of an unsymmetrical linkage of the type $R_1C \equiv CR_2$. Further peaks at 3000 cm^{-1} ($R_1CH = CHR_2$), 2925 cm^{-1}(-CH- and $-CH_2$), 3500 (free acid OH), and 1960 cm^{-1} (typical of an allenic system).

Chemical examination

On addition of ethanol to the pyrolysate, the red compound was precipitated as a viscous solid, which gave an infra red spectrum similar to that described above. Anhydride was proved to be present by the Davidson-Newman[63] test.

Ultra-violet examination

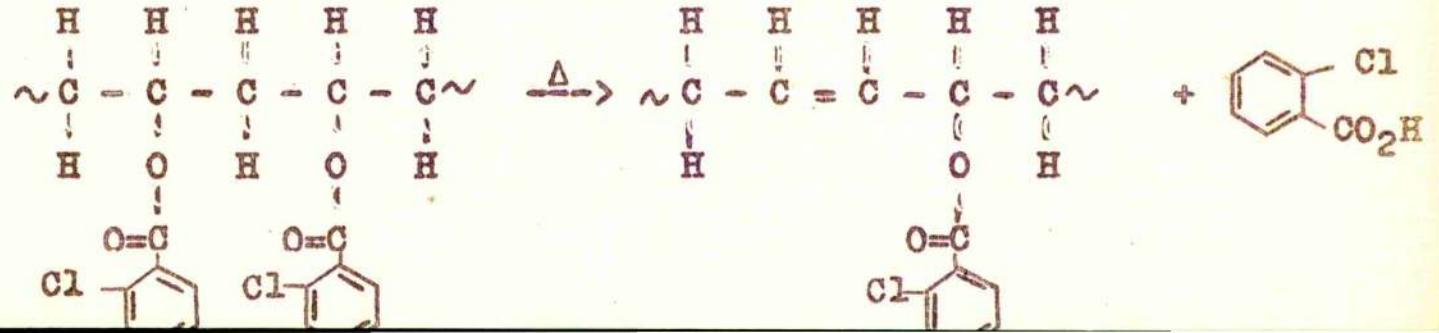
An ultra-violet spectrum of the compound in chloroform showed the presence of o-chlorobenzoic acid (impurity); further a series of small peaks centered at 540 mμ suggested the presence of a polyene with fourteen double bonds - this figure being suggested from work on carotenoids of similar chain lengths.

The presence of o-chlorobenzoic acid in the pyrolysate has therefore been firmly established, as has the absence of acetylene. Later work has shown that the evolution of acetylene does not become marked till ca. 400°. An anhydride and acetaldehyde have also been proved to be present.

4.3. Discussion

The following is suggested to account for all these facts. The first step involves the polymerisation by heat of the vinyl o-chlorobenzoate. The polymer so formed undergoes acid-stripping, yielding a polyene chain and o-chlorobenzoic acid. Grassie has found that liberation of acetic acid from polyvinyl acetate and the accompanying colouration is a molecular chain reaction in which initiation consists of the loss of a molecule of acetic acid from the saturated chain. The double bond so formed facilitates the loss of an adjacent acid molecule which is the propagation step and thus acid stripping is continued along the chain. It is proposed that acid stripping in poly(vinyl o-chlorobenzoate) proceeds by a similar mechanism, a view also put forward by Goodings[66] in work on the pyrolysis of poly(ethylene terephthalate). The acid so formed then reacts with unchanged monomer, forming ethylidene dichlorobenzoate which undergoes secondary breakdown to acetaldehyde and an anhydride. This scheme would also account for the large excess of acetaldehyde found in the pyrolysate from the four vinyl esters, which cannot be explained if the acid is formed only as a result of A^2 scission of the monomer.

The reaction scheme can be represented thus:



The reaction thus proceeds along the chain, forming a conjugated polyene having approximately fourteen double bonds.

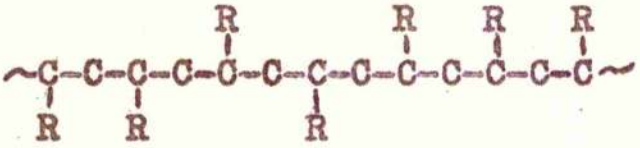
The overall reaction of the vinyl ester can be summarised by the following general scheme:

Monomer ----> Polyester ----> Acid + conjugated polyene

Anhydride + $CH_3.CHO$

4.3.1. Acetylenic Linkages

The above reaction scheme does not account for the acetylenic linkages detected by means of the infra-red spectrum. When the monomer polymerises, it will presumably do so in an atactic manner, with no stereoregulation along the backbone of the chain. The random configuration of the polyester can be represented thus:



R = $Cl.C_6H_4.CO_2$

The cis character of A^1 elimination has been shown by a number of experiments. In the simplest it has been shown that elimination does not take place in the absence of a cis β-hydrogen, or, at least, is so much slower than cis elimination as to imply the operation of another mechanism. Thus cis-2-methylcyclohexyl acetate gives mainly 3-methylcyclohexene[67], and cis-3-carbomethoxycyclohexyl

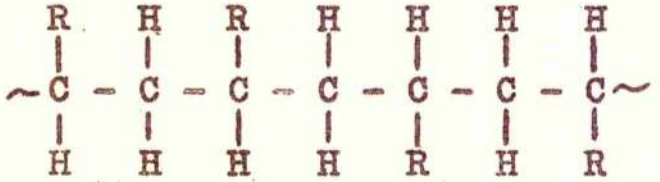
acetate exclusively 3-carbomethoxycyclohexene[68], on pyrolysis. Experiments using deuterated compounds have confirmed that the cis mode of elimination is the only mechanism possible.[69]

The structure of the chain, assuming that termination of the polymerisation is by disproportionation, will be:

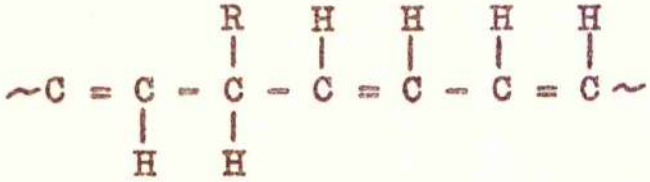
The bond energy D(CH-H) is ca. 98 k.cal., while D(=C-H) is 96 k.cal. Hence, there is no energy consideration to cause preferential elimination of a hydrogen atom linked to a saturated rather than an unsaturated carbon atom.

Acid stripping is autocatalytic[65]: hence assuming that in the above structural representation it proceeds solely from left to right, the final product will be a polyene terminated by a triple bond. This could account for the terminal RC ≡ CH grouping detected via the infra-red spectrum.

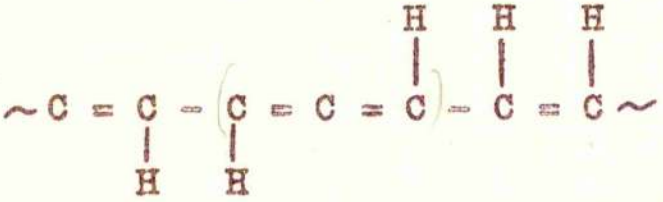
Similarly the polymer could formally lose acid from both ends simultaneously. Since it is atactic, a configuration such as the following may occur:



Hence, as acid stripping proceeds, an intermediate stage in the production of the polyene might be:



Because of the cis nature of the elimination, the next step would be loss of a further molecule of acid, resulting in an allenic linkage in the centre of the chain, thus:



This would probably isomerise immediately to the more stable acetylenic form, though a small amount might retain the above structure. This scheme would account for the peaks in the infra-red spectrum corresponding to $R_1C \equiv CR_2$ and the allenic linkage.

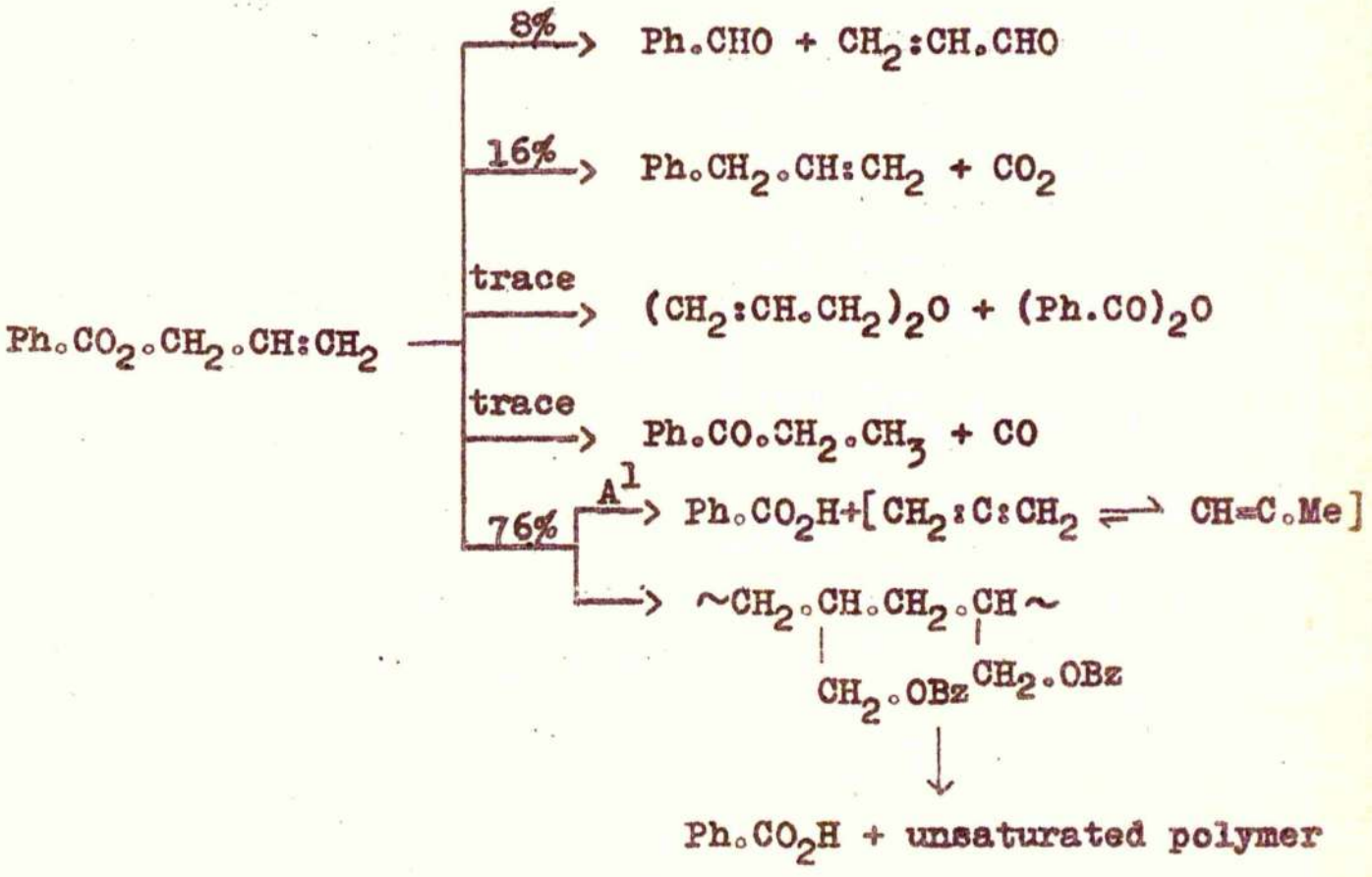
A sample of vinyl o-chlorobenzoate was polymerised (below 100°) in presence of 0.1% (molar) of benzoyl peroxide. The resulting polymer was then pyrolysed at 220°; again, a deep red colouration was detected in the pyrolysand and the presence of acetylenic linkages noted.

In previous work on the pyrolysis of allyl benzoate[13] ($Ph.CO_2.CH_2.CH = CH_2$) it had been reported that no allene or methylacetylene was found. If this was the case the result would have tended to show that the above reaction

schemes were improbable as an allyl-type structure is a postulated intermediate in the depolymerisation. If the allyl benzoates undergo A^1 scission then the allylic grouping in the polymer may also be assumed to undergo this scission. Accordingly allyl benzoate and allyl o-chlorobenzoate were pyrolysed with the results given below.

5.1. Pyrolysis of Allyl Benzoate

A sample of allyl benzoate was prepared and pyrolysed at 500°. The overall reaction scheme can be pepresented as:



In addition, benzene, toluene, water, ethylene, methane and hex-1-ene were detected.

The gaseous pyrolysate contained:

CO_2 = 52.5%

Unsaturated hydroc. = 19.0%

CO = 26.5%

CH_4 = 2.0%

5.2. Discussion of Results

Alkyl-oxygen scission of allyl benzoate has been demonstrated by the detection of methylacetylene. The extent of this A^1 scission is rather small and (just as in the pyrolysis of vinyl esters: see above) could not account for the large quantity of benzoic acid detected in the pyrolysate. A scheme similar to that proposed for the formation of benzoic acid from vinyl benzoate is therefore once more advanced; viz. polymerisation of the monomer followed by acid stripping of the resulting polyallyl benzoate.

However, the fact that A^1 scission has been proved to occur, even to a small extent, lends support to the suggested explanation of the formation of acetylenic linkages in the acid stripping of polyvinyl chlorobenzoate. It is interesting to note that though A^1 scission of the monomer occurs very slowly at this temperature alkyl-oxygen scission of the polymer is extremely facile. Polyvinyl acetate[65] has been shown to lose acetic acid at 200°. This may be due to activation of the β-hydrogen

by a conjugative effect thus facilitating the formation of acetic acid.

Allyl benzoate undergoes decarboxylation to allyl benzene, though the extent of this reaction is greater than in the vinyl esters. In contrast to this, B^2 scission of allyl benzoate, to benzaldehyde and acrolein has no parallel in the pyrolysis of vinyl benzoate. Here, the allyl group reacts more like an ethyl group which readily gives rise to acyl-oxygen scission in esters.

Rearrangement followed by decarbonylation (R/C^1) occurs to only a very minor extent, the product being propiophenone. This is probably due to the fact that the transition state as proposed by Young[49] cannot be attained without a prior rearrangement of the allyl ester to the isopropenyl form which is rather unlikely, although Muir[70] has shown that isopropenyl benzoate yields propiophenone on pyrolysis. Thus, the above scheme may proceed to a very small extent.

$$Ph.CO_2.CH_2.CH{=}CH_2 \xrightarrow{R} Ph.CO_2.CMe{=}CH_2 \xrightarrow{R} Ph.CO.CH_2.COMe$$

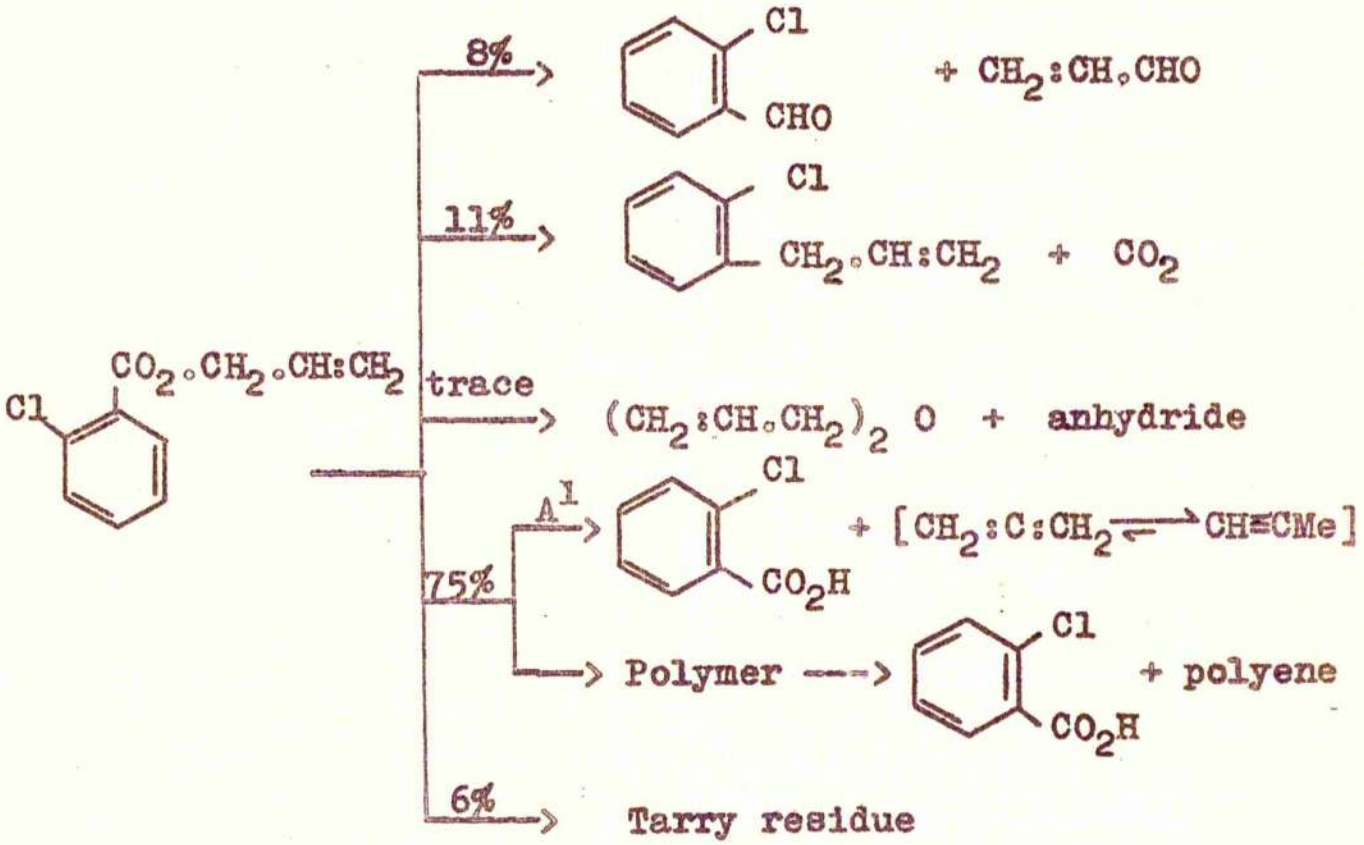
$$Ph.CO.CH_2.COMe \xrightarrow{\Delta\ C^1} Ph.CO.CH_2.CH_3 + CO$$

The formation of benzene follows the decarboxylation of benzoic acid and is a secondary reaction. Likewise, ethylene and carbon monoxide are decomposition products of the pyrolysis of acrolein.[71] At present, no satisfactory explanation can be advanced to account for the presence of

toluene, hex-1-ene and methane, though it is possible that some of these products at least, are formed by radical reactions.

5.3. Pyrolysis of Allyl o-chlorobenzoate

Allyl o-chlorobenzoate was pyrolysed at 500°. The various routes are as detailed below.



The gaseous pyrolysate contained:

CO_2 = 58.0%

Unsat. hydrocarbons = 21.6%

CO = 20.4%

Here, again, alkyl-oxygen scission has been deduced from the presence of methylacetylene in the gaseous pyrolysate. Allene is the actual product of A^1 scission, but this is

known to isomerise readily to methylacetylene on heating. Its extent is rather small, and most of the o-chlorobenzoic acid formed is assumed to arise from acid stripping of the polymer. A static pyrolysis confirmed that o-chlorobenzoic was formed without evolution of any gas and addition of methanol to the pyrolysate caused the precipitation of a viscous solid, presumably polymerised material. It is thought, therefore, that this type of reaction is one of the main routes in the pyrolysis of unsaturated esters and occurs to a far larger extent than alkyl-oxygen scission of the unsaturated monomer.

A B^2 scission occurs, the products being o-chlorobenzaldehyde and acrolein, there being no change in orientation from the parent ester. Decarboxylation (C^2) yields the o-chloroallylbenzene. A rearrangement (R) gives a trace of diallyl ether and an anhydride.

Secondary products include chlorobenzene, probably mainly from the decarboxylation of o-chlorobenzoic acid. Ethylene and carbon monoxide result from the decomposition of acrolein: some additional chlorobenzene and carbon monoxide may result from the decomposition of o-chlorobenzaldehyde. The presence of o-chlorotoluene, hex-1-ene and methane cannot at present be explained. An interesting point is that the infra-red spectra of the gaseous pyrolysates are almost identical in the cases of the two esters, viz. allyl benzoate and allyl o-chlorobenzoate.

6. Pyrolysis of p-chloroacetophenone

p-Chloroacetophenone had been detected as one of the main products in the pyrolysis of vinyl p-chlorobenzoate. It was decided, therefore, to study its pyrolysis (not previously recorded), which is a formally possible source of some of the secondary products detected in the pyrolysis of the ester.

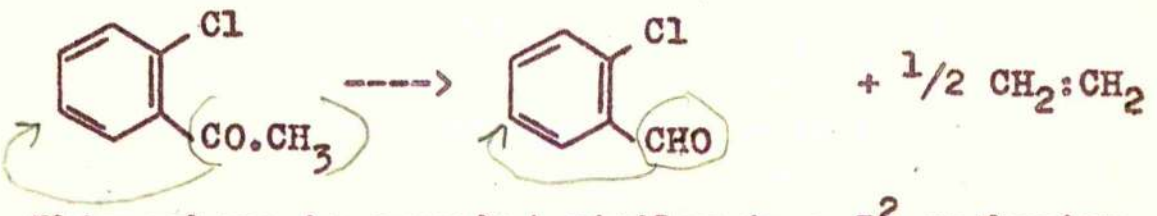
The pyrolysis of p-chloroacetophenone was carried out under conditions identical to those used for the ester but it was found that there was very little breakdown (only ca. 2%). Products isolated were p-chlorotoluene and chlorobenzene. The gaseous pyrolysate contained 96% CO and 4% methane. These results are in close agreement with those quoted by Hinshelwood[72] for the pyrolysis of acetophenone.

When the pyrolysis was repeated at 600°, the results were somewhat similar, but in addition to the compounds detected before, a small amount of p-chlorobenzaldehyde was found. The breakdown at this temperature was 4%. p-Chlorotoluene accounted for 55%, chlorobenzene 40% and p-chlorobenzaldehyde 5% of the actual breakdown. An infra-red spectrum of the gaseous pyrolysate showed the presence of carbon monoxide, ethylene and methane. Carbon monoxide can be accounted for in two ways.

(a) decarbonylation of p-chloroacetophenone to p-chlorotoluene,

(b) decarbonylation of p-chlorobenzaldehyde to chlorobenzene.

p-Chlorobenzaldehyde may be formed by the following mechanism, which also accounts for the presence of ethylene:



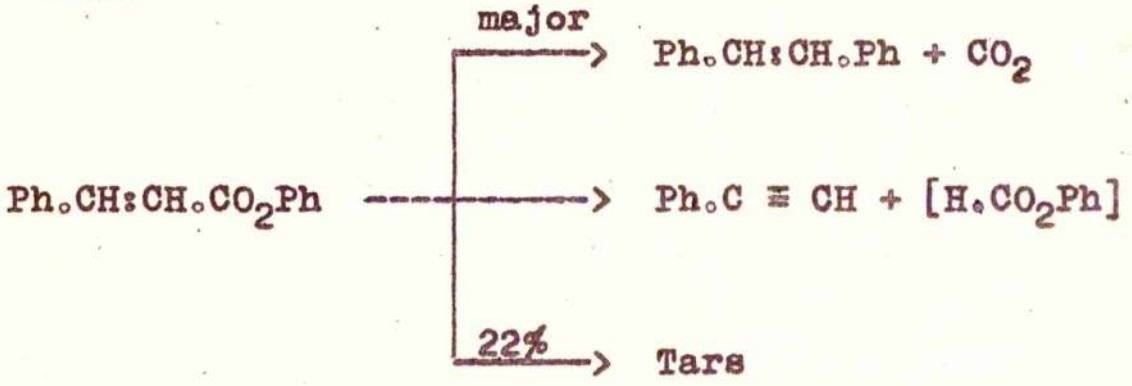
This scheme is somewhat similar to a B^2 mechanism.

The formation of toluene and the three chlorotoluenes in the pyrolysis of the vinyl esters therefore probably proceeds via the secondary decomposition of the acetophenones.

7.1. Pyrolysis of Phenyl Cinnamate

In the pyrolysis of phenyl acrylate (CH_2:CH.CO_2Ph), Mackinnon and Ritchie[14] detected a novel mode of scission to phenyl formate. They designated this as intra-acyl, since it involved a scission within the group CH_2:CH.CO. In an attempt to discover whether this is a general reaction in the pyrolysis of esters of type R.CH:CH.CO_2R', it was decided to pyrolyse phenyl cinnamate (R = R').

The competitive routes detected can be represented thus:



Secondary products detected were toluene, phenol, diphenyl (trace), dibenzyl, and anthracene.

The gaseous pyrolysate contained:

CO_2 = 55.0%

Unsat. hydrocarbons = 5.0%

CO = 40.0%

The major primary breakdown route shown above is decarboxylation (C^2) to trans-stilbene. Although there are three small unidentified peaks in the vapour phase chromatogram of the pyrolysate, the high yield of trans-stilbene (9.0 g. from 30.0 g. pyrolysand) suggests that the reaction cannot be radical in nature: if it were, the number of compounds detected in the pyrolysate would be far greater and would not lead to the almost exclusive production of trans-stilbene. The reaction, as previously postulated (Section 3.4.5.) must therefore be considered molecular. Also, Ritchie[14], found that the decarboxylation of phenyl acrylate was not affected by the addition of free-radical inhibitors to the pyrolysand.

The other major breakdown route is the intra-acyl scission, though occurring to a lesser extent than decarboxylation. Theoretically, the products from the scission should be phenylacetylene and phenyl formate. However, no trace of phenyl formate could be found, though its known decomposition products (phenol and carbon monoxide)[12] were detected in large quantities. Phenyl formate, pyrolysed under similar conditions, was found to break down completely to carbon monoxide and phenol with no trace of benzene.

Ritchie[14], showed that a B^1 reaction of the type $CH_2{:}CH{\cdot}CO{:}O{\cdot}Ph$, yielding phenol and a keten, was extremely unlikely; it is therefore assumed that the phenol arises from secondary breakdown of the phenyl formate. However, the accompanying phenylacetylene is much less than equivalent in amount to the observed carbon monoxide and phenol. This can be explained by secondary pyrolysis of the alkyne, with formation of much charred material and tar. Zelinski[73] noted that acetylene, passed over charcoal at 600°, yielded about 70% of tar and it is perhaps possible that the charred material in this type of reaction has a similar catalytic effect. Anthracene could thus be a product of the pyrolysis of phenylacetylene.

Ritchie[14] found that the intra-acyl scission is completely suppressed by the addition of quinol (1%) to the pyrolysand, which suggests that the breakdown is free radical in character. The observed traces of alkene in the gaseous pyrolysate and the compounds corresponding to the unidentified peaks in the chromatogram, may be accounted for as products of free radical mechanisms.

7.2. Pyrolysis of trans-stilbene

A separate pyrolysis of trans-stilbene was carried out under conditions similar to these in the pyrolysis of phenyl cinnamate, in an attempt to elucidate the formation of some of the secondary products detected in that pyrolysis.

Trans-stilbene proved very stable towards heat, only some 8% of the pyrolysand breaking down. No gas was evolved and there was only slight charring of material in the pyrolysis tube.

The sole product of decomposition was dibenzyl, a compound also detected in the pyrolysate of phenyl cinnamate. Its presence was confirmed by infra-red and vapour-phase chromatographic methods.

The only explanation of the presence of dibenzyl can be, that, on charring of some pyrolysand, protons are released. These immediately add across the double bond of trans-stilbene, thus forming dibenzyl. No other products of decomposition could be detected; nor can the pyrolysis of trans-stilbene be responsible for the tar formation detected in the previous pyrolysis.

8. Co-pyrolysis of phenyl fumarate and 4-4' chlorophenyl maleate.

These two esters were co-pyrolysed in an attempt to elucidate the mechanism of decarboxylation (C^2).

Phenyl fumarate on pyrolysis yields trans-stilbene and 4-4' chlorophenyl maleate gives 4-4' dichloro-stilbene, as below:-

(a) $$\begin{matrix} Ph.O_2C.CH \\ \| \\ Ph.O_2C.CH \end{matrix} \xrightarrow[C^2]{\Delta} \begin{matrix} Ph.CH \\ \| \\ Ph.CH \end{matrix} + 2\ CO_2$$

(b) $$\begin{matrix} Cl.C_6H_4.O_2C.CH \\ \| \\ Cl.C_6H_4.O_2C.CH \end{matrix} \xrightarrow[C^2]{\Delta} \begin{matrix} Cl.C_6H_4.CH \\ \| \\ Cl.C_6H_4.CH \end{matrix} + 2\ CO_2$$

If this reaction proceeds by a radical mechanism, some of the products which may be expected on pyrolysis, apart from those mentioned in (a) and (b) above, are diphenyl, 4-4' dichlorodiphenyl and 4-chlorostilbene. However, should the reaction proceed by an intramolecular mechanism, the sole primary products of decarboxylation should be trans-stilbene and 4-4' dichlorostilbene.

On co-pyrolysis in the flow system considerable charring was noted when the compounds were pyrolysed at 500°. After several trial runs in the static pyrolysis apparatus it was found that the most suitable temperature for clean pyrolysis was 340°, ca. 40° above the temperature of initial decarboxylation.

Four compounds were detected in the pyrolysate: these were trans-stilbene, 4-chlorostilbene, 4-4' dichlorostilbene and phenyl cinnamate. There was no trace of any other breakdown product.

The composition (%) of the pyrolysand was:

4-4' dichlorostilbene	49.5
trans-stilbene	21.5
phenyl cinnamate	28.0
4-chlorostilbene	1.0

The presence of 4-chlorostilbene might tend to indicate a radical mechanism, but as the quantity formed is so small and no other products which might be expected from a radical reaction were detected, this mechanism is at best unlikely. A more likely explanation of the occurrence of 4-chlorostilbene is via decarboxylation of 4-chlorophenyl maleate, formed by ester interchange previous to pyrolysis. This is possible, as in the apparatus used (described in Part II) a static system was employed and the temperature was only gradually raised to 340° before being maintained there. Thus:

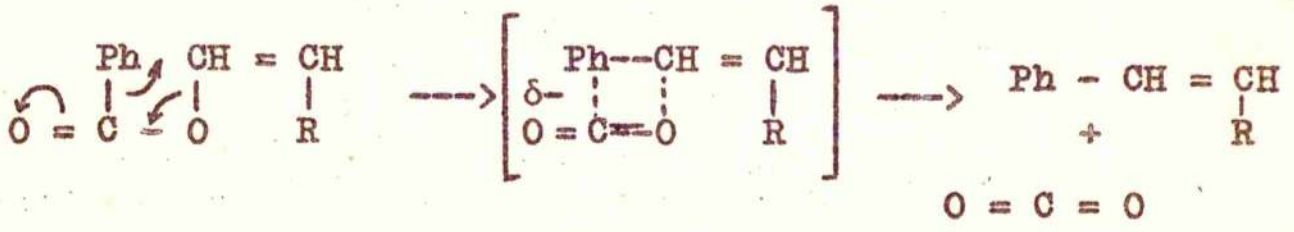
$$(Cl.C_6H_4.O_2C.CH:)_2 + (Ph.O_2C.CH:)_2 \longrightarrow Ph.O_2C.CH{=}CH.CO_2.C_6H_4Cl$$

$$\xrightarrow[340^\circ]{\Delta\ C^2}$$

$$Ph.CH{:}CH.C_6H_4.Cl.$$

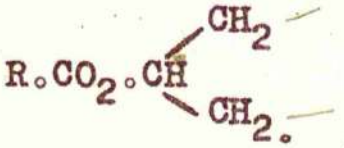
The main decarboxylation is therefore thought to proceed via an intramolecular mechanism (as previously postulated)

with the ester group at no time becoming detached from the main body of the molecule. The mechanism can be shown as:



9. Pyrolysis of iso-propyl benzoate

Muir[70] has found that cyclohexyl benzoate decomposes at temperatures between 300 - 530° by an exclusive A^1 alkyl-oxygen scission to benzoic acid and cyclohexene. No acyl-oxygen scission could be detected. However, on the addition of metal catalysts to the pyrolysand, a variety of products were obtained including compounds which could be explained by a B^2 scission. B^2 scission is therefore not structurally ruled out. Barton[10] has found that (-)-menthyl benzoate also breaks down exclusively by an A^1 scission. Both these esters have the common structure

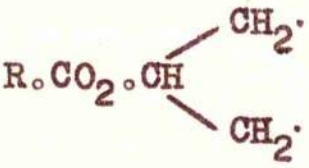


In an attempt to discover whether this one-route breakdown is general in esters of this type, it was decided to pyrolyse isopropyl benzoate, $Ph.CO_2CH(Me)_2$.

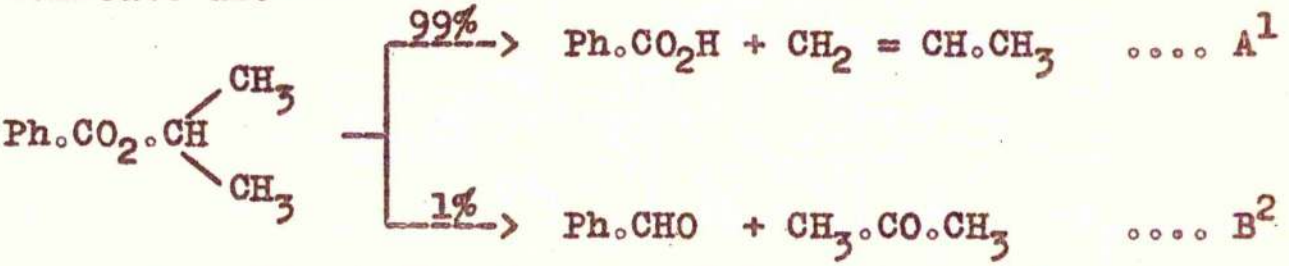
This compound was pyrolysed at 500°. Decomposition was 100%, the products of pyrolysis being almost exclusively benzoic acid and propene. However, a slight trace of

benzaldehyde was detected in the pyrolysate and an infra-red spectrum of the gas showed a small peak at 1724 cm. which is characteristic of the C = O group in acetone. Thus, though probably 99% of the pyrolysis proceeds <u>via</u> an alkyl-oxygen scission, a very small amount of acyl-oxygen (B^2) scission also occurs. The bezaldehyde was detected on a "Pye Argon" chromatograph: it is possible that previous workers, through using less sensitive equipment, failed to detect similar minor products.

In this connection it is interesting to note that cyclohex-1-enyl benzoate[56] pyrolyses by three primary routes, isopropenyl benzoate[70] by three primary routes and benzyl benzoate[74], amongst other products, yields benzaldehyde.

From this, it seems therefore, that esters containing the grouping  pyrolyse almost exclusively by one route, namely alkyl-oxygen scission. There is no obvious reason for this and further work is necessary.

The overall scheme for the pyrolysis of isopropyl benzoate is:-



A small sample of n-propyl benzoate was found to undergo a B^2 scission to benzaldehyde and propionaldehyde in the region of 400°.

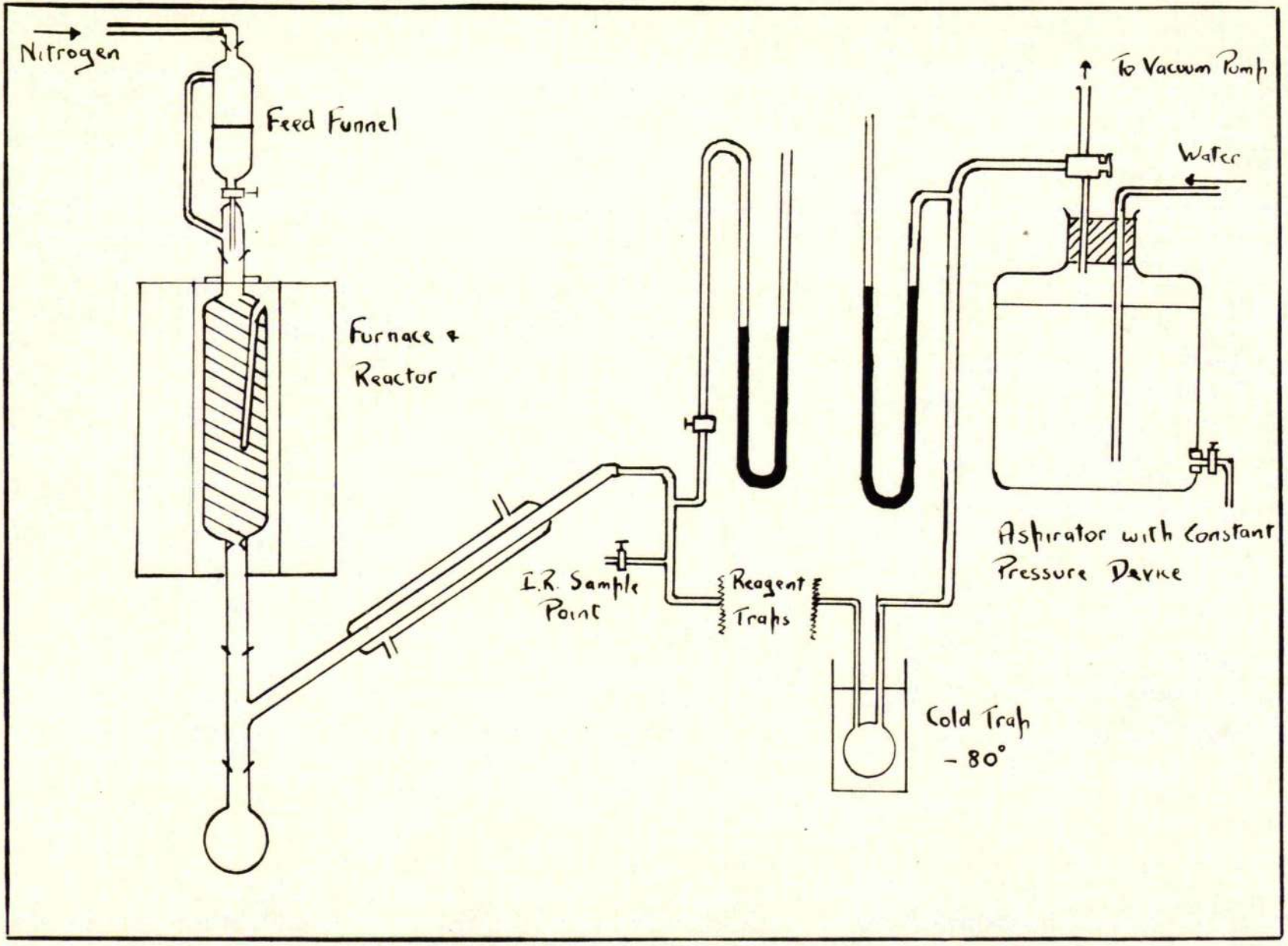
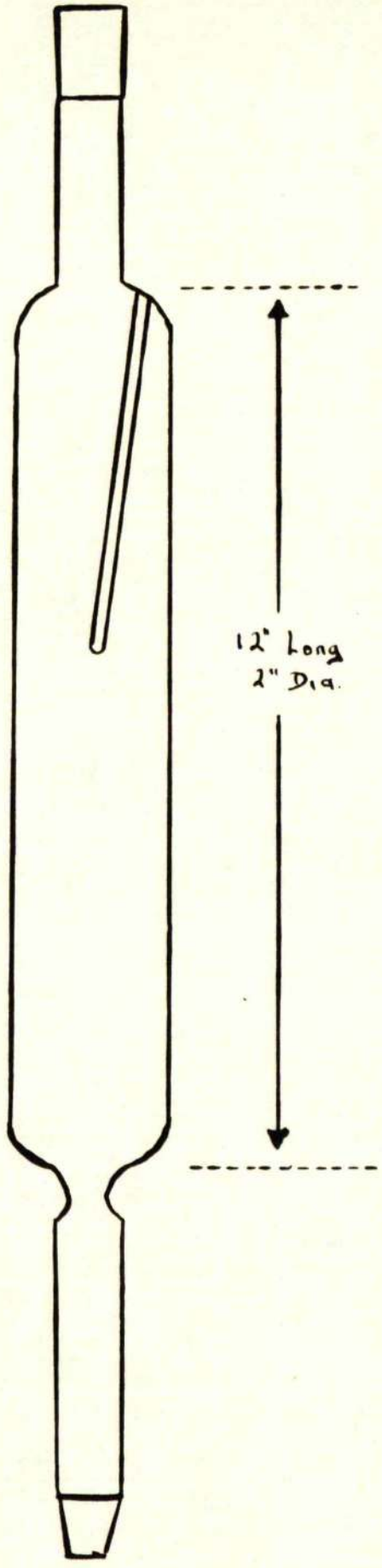

Nitrogen
Feed Funnel
Furnace + Reactor
I.R. Sample Point
Reagent Traps
Cold Trap -80°
To Vacuum Pump
Water
Aspirator with Constant Pressure Device

FIG. 5



Reactor
Volume
270 c.c.

FIG. 6

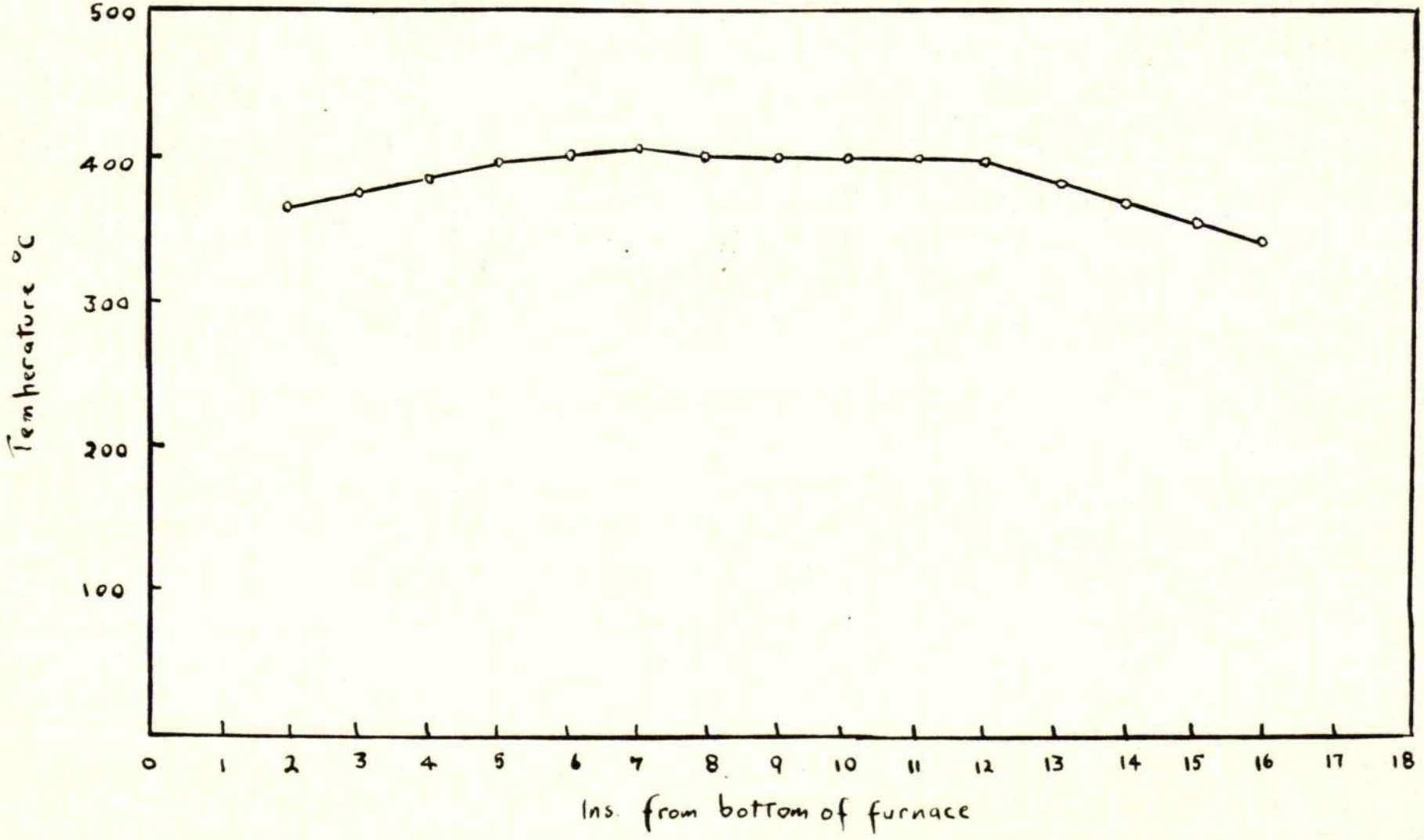

500
400
300
200
100
Temperature °C
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Ins. from bottom of furnace

FIG. 7

10. Experimental

10.1 Apparatus

All pyrolyses were carried out in a flow system as illustrated in Fig.5. An atmosphere of dry, oxygen free nitrogen was used throughout. The pyrolysand was admitted to the top of the reactor, the rate of addition being carefully controlled. Solid pyrolysands were liquified before addition by means of an electrically heated tape wound round the container. The products were separated into rough fractions as they emerged from the column, solids and liquids being retained at the foot of the reactor, low boiling liquids being condensed at - 80° and gases being collected in a constant pressure receiver.

The pyrolysis column was housed in a thermostatically regulated furnace, the ends of which were tightly packed with asbestos to prevent the formation of convection currents. The column itself was 12 ins. long, 2 ins. in diameter and constructed of Pyrex glass (Fig.6): a thermocouple pocket was sealed into the column, long enough to reach the region of maximum temperature. The reactor was packed with $^1/_2$ ins. lengths of 7 mm. diameter Pyrex tubing giving a reaction volume of 270 cm^3. The temperature of pyrolysis was regarded as the maximum temperature attained in the reactor, the temperature being maintained to $\pm 5°$ of this value. The correct position for the chrome-alumel thermocouple was obtained from the temperature distribution curve (Fig.7).

The pyrolysand was fed to the reactor from a dropping funnel fitted with a pressure balancing arm. Solid and liquid products of the pyrolysis were then condensed together at the foot of the reactor, firstly by an air condenser and then by a water condenser. In certain pyrolyses reagent traps were used in the system, so that volatile aldehydes (2:4 dinitrophenylhydrazine in 2N-HCl trap) or ketens (aniline trap) could be removed. Low boiling liquids were then condensed in an acetone/Drikold trap before the gases were taken to the constant pressure receiver. This receiver was maintained at atmospheric pressure and was filled with water covered by a layer of paraffin oil to prevent absorption of the gases. Mercury manometers were used to indicate pressure in the system and a three way tap was incorporated to allow gas samples to be removed for infra-red analysis during the course of the pyrolysis.

Before runs, the apparatus was evacuated to low pressure, brought back to atmospheric pressure with nitrogen and then flushed out with more nitrogen. This was repeated several times, the apparatus finally being filled with nitrogen to ca. 1 mm. above atmospheric pressure.

Flow rates have been found to effect the extent of decomposition. Therefore residence times have been calculated from the formula given by Barton[75].

$$\text{Residence time} = \frac{3600 \times 273 \times Vc}{22{,}400 \times (N_R + N_{N_2}) \times T}$$

Vc = contact volume

N_R = moles pyrolysand/hr.

N_{N_2} = moles N_2/hr (= zero)

T = absolute temp. °K

The reactor was cleaned after each run by burning in a stream of air. This normally removed all traces of carbonisation and no further cleaning measures were required.

10.2 Analysis Methods

Paper chromatography

Paper chromatography was used for the separation and identification of aldehydes, the method used being that according to Burton[76] in which the liquid phase is a 12:3:1 mixture of methanol-water-ethyl tartrate. This system proved very convenient for an indication of the number of aldehydes present, and, by the use of standards, a useful pointer to their identification.

Gas-Liquid Chromatography

Two different commercially available machines were used: initially a Griffin and George Mark IIB and latterly a Pye "Argon" fitted with integrator.

The time taken for a substance, under standard conditions to pass through a particular gas-liquid column is a characteristic property of the substance which can be used

to identify it. The use of retention times for characterisation has several important advantages. A retention time is almost completely independent of the purity of the sample. Different retention times may be obtained by passing the substance through the column at different temperatures and pressures. Thus, by careful use of standards, unknown substances in a mixture can be readily identified.

For vapours having similar thermal conductivities the area under the peak gives an approximate measure of the weight present. For both the Griffin and George, and Pye chromatographs, quantitative results were obtained by passing mixed standards of known composition through the machine and analysing the resultant peak areas. The results so obtained were then applied to actual pyrolysates. Extremely accurate analysis is not possible, but a good indication of relative proportions can be obtained by this method.

Infra-red spectrometer

A Perkin-Elmer "Infracord" instrument was used. For samples requiring greater resolution, use was made of a Grubb-Parsons spectrometer.

Identification of pure compounds was established by the use of standards. In mixtures, a guide to the identities of various constituent groups and orientation of isomers could be obtained from a study of the resultant spectra. The composition of gases from the pyrolysate could be readily established from the characteristic peaks of each, again

using standards. However, in mixtures of liquids of too great complexity, this method was not of much assistance.

Analysis

Liquid products were subjected to fractionation: any solid present in the pyrolysate was filtered off and purified. Chemical methods of identification were used and supplemented by the methods above. Cold trap liquids were allowed to evaporate off into a gas cell and analysed on the infra-red spectrometer. A standard Hempel apparatus was used for gas analysis with the addition of a potassium iodomercurate pipette for acetylene analysis[77].

11. Preparation and purification of pyrolysands

11.1. Vinyl o-chlorobenzoate was prepared by the ester interchange method as described by Ham and Ringwald.[78]

1 mole o-chlorobenzoic acid, 2 moles freshly dried and distilled vinyl acetate, 3.2 g. mercuric acetate and 0.3 ml. conc. sulphuric acid were refluxed with constant stirring on a water bath for 60 hours. The mixture was then distilled and the fraction boiling at 110-112°/9 mm. collected. This was purified by distillation through a 12 ins. Vigreux column, the final product having a boiling point of 113°/11 mm. [lit. 115°/12 mm.]. The purity was confirmed on the vapour phase chromatograph.

Yield 50 g. = 28%

Found	C = 59.3	H = 4.1	Cl = 20.7
Calc.	C = 59.3	H = 3.9	Cl = 19.5

11.2. Vinyl p-chlorobenzoate was prepared by a similar method. The fraction, boiling range 106-110°/9 mm., was collected and allowed to crystallise. The solid was recrystallised from an alcohol-water mixture and white, needle shaped crystals were obtained, m.p. 49°.

Yield 47 g. = 26%

Found	C = 58.9	H = 4.1	Cl = 19.4
Calc.	C = 59.3	H = 3.9	Cl = 19.5

11.3. Vinyl m-chlorobenzoate was obtained in fair yield using the ester interchange method. The fraction boiling at 100-110°/9 mm. was collected and further fractionated three times through a 12 ins. Vigreux column. The fraction boiling 104°/8 mm. was used for pyrolysis amd its purity was established by vapour phase chromatography.

The yield was 46 g. = 26%

Found C = 59.1 H = 4.2 Cl = 19.3

Calc. C = 59.3 H = 3.9 Cl = 19.5

In all three esters, the yields from several preparations were combined.

Vinyl benzoate was kindly donated by W. Muir.

11.4. Keten was prepared by the breakdown of acetic anhydride at 500°. The apparatus consisted of an acetic anhydride holder, a temperature controlled furnace, Drikold traps for removing acetic acid and unchanged anhydride and a liquid nitrogen trap for collection of the keten. The whole apparatus was used at 1 mm. Hg. pressure.

The keten was purified by two distillations and finally collected in a receiver which contained frozen benzene. On warming up, the keten was thus dissolved in the benzene.

11.5. Phenyl cinnamate was synthesised according to the preparation of Womack and McWhirter.[79]

The acid chloride was prepared by heating $^{2}/_{3}$ mole of cinnamic acid with an excess of thionyl chloride. When evolution of HCl had ceased 0.7 mol phenol was added and the mixture again heated till evolution of HCl ceased. The mixture was fractionated and the fraction boiling 190-220°/15mm collected. It was purified by grinding in a motar , extracting with sod. bicarbonate and finally recrystallised from 95% ethanol. White crystals (m.p. 75° were obtained [lit.75-76°].

Found	C	= 80.8	H	= 5.5
Calc.	C	= 80.4	H	= 5.4

11.6. Phenyl formate was produced by the action of 63 g. phenol and 152 g. phosphoryl chloride on 150 g. formic acid (90^{W}/w%). 2g. aluminium chloride was added to the reaction mixture and the whole allowed to stand at room temperature for 1 hour. The mixture was then heated at 80° for 5 hours. The product was extracted with ice-cold water, taken up in ether and dried. Phenyl formate was distilled over at 81-83°/15 mm. The final product proved negative for phenol. Yield was 28 g. = 7%.

Found	C	= 69.10	H	= 4.92
Calc.	C	= 68.90	H	= 5.30

11.7. Phenyl Maleate. Several methods were tried unsuccessfully for the preparation of phenyl maleate. Among them were the methods of Bischoff and Hedenstrom[80], and Bader and Kontowicz[81] using polyphosphoric acid as catalyst. Eventually, the following method was used:

48 g. phenol was dissolved in 400 ml. water containing 27 g. sod. carbonate. 50 g. maleic anhydride was then slowly mixed in and the monophenyl ester precipitated with HCl. 26 g. monophenyl ester was then added to 30 g. thionyl chloride and the mixture heated on a steam bath for an hour. Excess thionyl chloride was removed, 15 g. phenol added, and the mixture heated for 4 hours. On cooling, a solid separated out and was recrystallised from toluene-heptane, m.p. 162-3°. This is near the m.p. of phenyl fumarate [163°]: it was therefore thought the compound obtained had isomerised. Phenyl fumarate was confirmed by I.R. analysis [peak at 975 cm^{-1} which corresponds to a trans configuration]. However, for the purposes of the pyrolysis, the configuration did not matter.

Found	C = 71.5		H = 4.8		
Calc.	C = 71.7		H = 4.5		

11.8. 4-4' dichlorophenylmaleate was prepared by the same method. However, the cis configuration was retained. White crystals, recrystallised from toluene - heptane were obtained, m.p. 111°.

Found	C = 56.6		H = 3.2	Cl = 21.15	
Calc.	C = 57.0		H = 3.0	Cl = 21.05	

11.9. Allyl benzoate was prepared according to the method suggested by Perkin.[82]

140 g. benzoyl chloride and 116 g. allyl alcohol were heated in a water bath till evolution of HCl had ceased. The product was extracted with ether, washed with sod. carbonate and water, dried and distilled. It was refractionated through a Vigreux column and the fraction boiling 88-90°/5 mm. collected. Yield = 100 g.

Calc. C = 74.1 H = 6.2

Found C = 74.0 H = 6.4

11.10. Allyl o-chlorobenzoate was prepared in the same way using 70 g. o-chlorobenzoic acid and 90 g. thionyl chloride: 60 g. allyl alcohol was then added to the acid chloride. The product was extracted as before and the fraction boiling 125°/9 mm. collected. Vapour phase chromatography showed the presence of only one compound.

Found C = 61.7 H = 4.9 Cl = 17.4

Calc. C = 61.2 H = 4.7 Cl = 17.8

11.11. Iso-propyl benzoate was prepared by refluxing 60 g. benzoic acid, 75 ml. isopropyl alcohol (Analar), 5 ml. conc. sulphuric acid and 100 ml. benzene. The product was washed and extracted in the usual manner. It was purified by distilling through a Vigreux column and the fraction boiling 80-82°/5mm. collected. Yield = 60.0 g.

Found C = 72.7 H = 7.2

Calc. C = 73.0 H = 7.3

11.12. p-chloroacetophenone was prepared as described by Adams and Noller.[83]

A mixture of 28 g. chlorobenzene, 100 ml. carbon disulphide, 75 g. anhydrous aluminium chloride and 21 g. acetic anhydride was slowly refluxed. The carbon disulphide was then distilled off and the remainder poured over cracked ice to which HCl had been added. The mixture was extracted with ether, washed with 10% sod. hydroxide, and water. Finally, p-chloroacetophenone was distilled over at 124-126°/24 mm. The compound was refractionated. Yield was 20 g. = 50%. Later samples of p-chloroacetophenone were obtained from Messrs. Eastman Kodak.

12. Preparation of Standards

12.1. m-chloroacetophenone is obtained by means of diazotisation of m-aminoacetophenone.[84]

15 g. m-aminoacetophenone was diazotised with 8 g. sodium nitrite in the usual manner, and added to a warm, freshly prepared solution of cuprous chloride in 5N HCl. The mixture was steam distilled, extracted with ether, washed with sod. carbonate, dilute HCl, and finally dried. The compound was then distilled over, boiling point 113°/11 mm.

12.2. 4-chlorostilbene was prepared as described by Bergman[85]. A solution of 30 g. p-chloroaniline in 100 ml. water and 80 ml. conc. HCl was diazotised. The diazo solution was added to a cooled solution of 30 g. cinnamic acid in 250 ml. acetone. After addition and solution of 44 g. sodium acetate, a freshly prepared solution of 8.5 g. cuprous chloride in 20 ml. water was added. The mixture was then steam distilled and the residue taken up in benzene, washed with 3N ammonium hydroxide and water. The solvent was removed and a crystalline residue was obtained. The 4-chlorostilbene was recrystallised from isopropanol. m.p. 128° [Lit.129°].

12.3. Phenylacetylene was prepared as described by Fusschman and Sasse.[86] Styrene was first brominated, then the compound so formed was treated with methanolic pot. hydroxide. The solution was boiled for one hour, the alcohol

removed and water added. This was extracted with ether and distilled over solid pot. hydroxide. Phenylacetylene was collected at 137-9°.

12.4. 4-4' dichlorostilbene was prepared using a Grignard type reaction as suggested by Lints[87]. Quantities were calculated according to the paper by Graham.[88]

A solution of 100 g. 4-chlorobenzyl chloride in 500 ml. dry ether was added to 30 g. magnesium, 1 crystal iodine and 50 ml. anhydrous ether. The mixture was stirred and heated. 80 g. p-chlorobenzaldehyde was then added and the mixture again heated. The solution was then hydrolysed with dilute acetic acid, washed with sodium hydroxide, and sodium bisulphite. The ether was evaporated off and the alcohol heated with 1 ml. 48% H Br at 230° for 20 min. until evolution of water had ceased. The product was distilled at 215-230°/10 mm. and the crude product re-crystallised from toluene. m.p. = 174° [Lit. 175-6°].

All other standards were obtained commercially.

13. Summary of Results

A summary of the results is given overleaf.

Unless otherwise stated, all solid pyrolysates, components (or solid derivatives) mentioned below were identified by mixed melting point tests, agreeing ($\pm 1°$) with the observed and/or recorded melting point of the pure compound.

The following abbreviations are used in this section:

2:4 DNP(a)	=	2:4 dinitrophenylhydrazine
2:4 DNP	=	2:4 dinitrophenylhydrazone
VPC	=	vapour phase chromatography
IR	=	infra-red
UV	=	ultra-violet
m.p.	=	melting point

Pyrolysand	Vinyl o-chlorobenzoate			Vinyl m-chlorobenzoate		Vinyl p-chlorobenzoate	
Pyrolysis No.	1	2	3	4	5	6	7
Temperature	500°C	500°	500°	500°	500°	500°	500°
Feed rate (g./min.)	0.31	0.33	0.21	0.29	0.30	0.35	0.31
Residence time (sec.)	150	142	222	159	154	134	150
Weight pyrolysed (g.)	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Pyrolysate (a) In main receiver(g.)	21.0	20.0	21.0	19.5	21.0	20.0	21.0
(b) Gaseous (l.)	4.2	4.3	4.5	4.2	4.2	4.4	4.0
Composition (%) of (b)							
Carbon Monoxide	76.0	76.0	-	80.5	81.5	79.5	79.5
Carbon Dioxide	17.0	18.0	-	9.0	9.0	13.0	13.0
Acetylene	4.0	3.0	-	8.0	7.0	5.5	5.5
Unsat. hydrocarbons	3.0	3.0	-	2.5	2.5	2.0	2.0
Sat. hydrocarbons	trace	trace	-	trace	trace	trace	trace
Ester unchanged (g.)	3.5	3.7		3.0		3.0	

Pyrolysand	Vinyl benzoate	Allyl benzoate	Allyl o-chlorobenzoate	p-Chloro-acetophenone
Pyrolysis No.	8	9	10	11
Temperature	500°	500°	500°	600°
Feed rate (g./min)	0.28	0.21	0.25	0.38
Residence time (sec.)	135	195	198	92
Weight pyrolysed (g.)	30.0	20.0	20.0	30.0
Pyrolysate		Cold trap 1.0g.	Cold trap 2.0g.	
(a) In main receiver(g.)	24.0	15.0	15.0	29.0
(b) Gaseous (l)	3.3	3.0	2.4	1.0
Composition (%) of (b)				
Carbon monoxide	80.0	26.5	20.4	95.0
Carbon dioxide	14.0	52.5	58.0	-
Acetylene	3.0	-	-	-
Unsat. hydrocarbons	3.0	19.0	21.6	3.0
Sat. hydrocarbons	trace	2.0	-	2.0
Ester unchanged (g.)	7.3	10.0	5.6	28.0

Pyrolysand	p-Chloroaceto-phenone	Phenyl cinnamate	Phenyl formate	trans-Stilbene	Isopropyl benzoate
Pyrolysis No.	12	13	14	15	16
Temperature	500	500	500	500	500
Feed rate (g./min.)	0.25	0.35	0.32	0.37	0.33
Residence time (sec)	92	153	116	125	138
Weight pyrolysed (g.)	20.0	30.0	15.0	10.0	20.0
Pyrolysate					
(a) In main receiver(g.)	19.0	22.0	11.0	8.0	Cold trap 40g. 14.0
(b) Gaseous (l.)	0.2	2.8	2.8	0.0	0.8
Composition (%) of (b)					
Carbon monoxide	96.0	40.0	99.0	0.0	0.2
Carbon dioxide	-	55.0	1.0	0.0	6.0
Unsat. hydrocarbons	-	5.0	-	0.0	93.8
Sat. hydrocarbons	4.0	-	-	0.0	-
Ester unchanged (g.)	19.0	3.0	0.0	9.0	0.0

Pyrolyses 1, 2 and 3.

2:4 DNP (a)/2N-HCl trap contained orange precipitate in each case. On recrystallisation gave m.p. 157°. Single compound proved by paper chromatography and mixed m.p. to be acetaldehyde derivatives.

IR spectrum of gas shows presence of acetylene, ethylene and methane.

Solid fraction filtered off. 1.2g.(Run 1) 1.0g.(Run 2)

Dissolved in sod. carbonate, precipitated with HCl; recrystallised from water; o-chlorobenzoic acid (m.p. and mixed m.p. 140°).

Cold trap: water formed in both runs ($CuSO_4$ test).

	Pyrolysis 1	Pyrolysis 2
Initial fractionation:		
(i)	20-88°/4mm - 7g.	24-64°/5mm - 6g.
(ii)	88-96°/7mm - 8g.	64-84°/4mm - 6g.
(iii)	92°/5mm - 3g.	84-104°/4mm- 4g.
(iv)	- -	110°/4mm - 0.3g.
	Residue > 92°/5mm - 3g.	> 110/4mm - 3g.

Fract. (ii) gave 2:4 DNP of o-chloroacetophenone (m.p. and mixed m.p. 206°). Paper chromatography shows presence of only one carbonyl compound.

VPC was not applied to pyrolysis 1.

Pyrolysis 2 - fract. (i) redistilled to give 0.4g. fract.(i)a and 5.6g. fract.(i)b.

Fract.(i)a had an IR spectrum identical to that of chlorobenzene. VPC was used on fract.(i)b and (ii). Standard retention times were obtained by the author and are not from the literature.

Column 30% Silicone E.301 on Celite.

Temp.° 166°

N_2 flow 1.2 l./hr.

Inlet press. 526 mm.

Outlet press. 165 mm.

Fraction times(i)b retention times(min.)	Standard retention times (min.)	
3.7	Chlorobenzene	3.7
5.1	o-Chlorotoluene	5.1
6.0(minor)	-	
8.0	o-Chlorostyrene	8.0
10.1	o-Chlorobenzaldehyde	10.1
14.0	o-Chloroacetophenone	14.0
21.5	Vinyl o-chlorobenzoate	21.6
	m and p-Chlorostyrene	8.5
	p-Chloroacetophenone	17.4
	m-Chloroacetophenone	18.0

Fraction times(ii) retention times(min.)	Standard retention times (min.)	
14.0	o-Chloroacetophenone	14.0
21.5	Vinyl o-chlorobenzoate	21.5

Column	10% Silicone E.301 on Celite
Temp.°	176°
N_2 flow	2.8 l./hr.
Inlet press.	620 mm.
Outlet press.	208 mm.

Fraction times(i)b retention times(min.)	Standard retention times (min.)	
1.1	Chlorobenzene	1.1
1.5	o-Chlorotoluene	1.5
2.0(minor)	-	
2.2	o-Chlorostyrene	2.2
2.8	o-Chlorobenzaldehyde	2.8
3.5	o-Chloroacetophenone	3.6
5.5	Vinyl o-chlorobenzoate	5.5

Fraction times(ii) retention times (min.)	Standard retention times (min.)	
3.6	o-Chloroacetophenone	3.6
5.5	Vinyl o-chlorobenzoate	5.5

o-Chloroacetophenone confirmed by 2:4 DNP m.p. and mixed m.p. 206°.

Fracts. (ii) and (iii) gave identical peaks though in fract. (iii) vinyl o-chlorobenzoate accounted for the major proportion.

Fract.(iv) recrystallised from water: o-chlorobenzoic acid (m.p. and mixed m.p. 139°).

Residue extracted with sod. carbonate, precipitated with acid. Recrystallised from water. White crystals m.p.139°: o-chlorobenzoic acid, confirmed by mixed m.p.

Test for anhydride positive (Davidson - Newman).

IR spectrum fract.(i)b: further fractionated into two groups, 50-53°/4mm and 53-62°/4mm., show no trace of any m- or p-chlorostyrene. Presence of o-chlorostyrene confirmed.

Pyrolysis 3

The pyrolysate was not fractionated, the main purpose of the run being simply to show the presence or absence of keten (aniline-ether trap). This, however, proved unsuccessful though o-chlorobenzaldehyde was detected. VPC showed presence of same compounds as previously detected, though on this occasion no o-chlorotoluene was detected.

Column 30% Silicone E.301 on Celite

Temp.° 168°

Flow 1.3 l./hr.

Inlet press. 555 mm.

Outlet press. 188 mm.

Peaks at 3.6, 8.4, 10.5, 13.9 and 21.2 min.

Standards: chlorobenzene 3.5, o-chlorostyrene 8.4, o-chlorobenzaldehyde 10.4, o-chloroacetophenone 13.9 and vinyl o-chlorobenzoate 21.2 min.

Pyrolyses 4 and 5

On each run, 2:4 DNP(a) trap yielded orange derivative: on recrystallisation m.p. 160°. Mixed m.p. acetaldehyde derivative 160°. Paper chromatography confirmed presence of only one compound.

Cold trap: water formed in both runs ($CuSO_4$ test)

	Run 4	Run 5
Solid fraction filtered off.	4.5g.	-
Liquid pyrolysate.	15.0g.	21.0g.

Solid recrystallised from water: m-chlorobenzoic acid (m.p. and mixed m.p. 148°).

The liquid pyrolysate was fractionated (Pyrolysis 5, liquid and solid).

	Pyrolysis 4	Pyrolysis 5
(i)	20-68°/5mm. - 1.5g.	22-66°/4mm. - 1.5g.
(ii)	68-84°/5mm. - 6g.	66-80°/4mm. - 12g.
(iii)	84-108°/5mm. - 7.5g.	80-86°/4mm. - 2.5g.
Residue	None	> 86°/4mm. - 4.8g.

Fract.(ii) (both runs) yielded the semicarbazide of m-chloroacetophenone (m.p. and mixed m.p. 232°: lit. 232°).

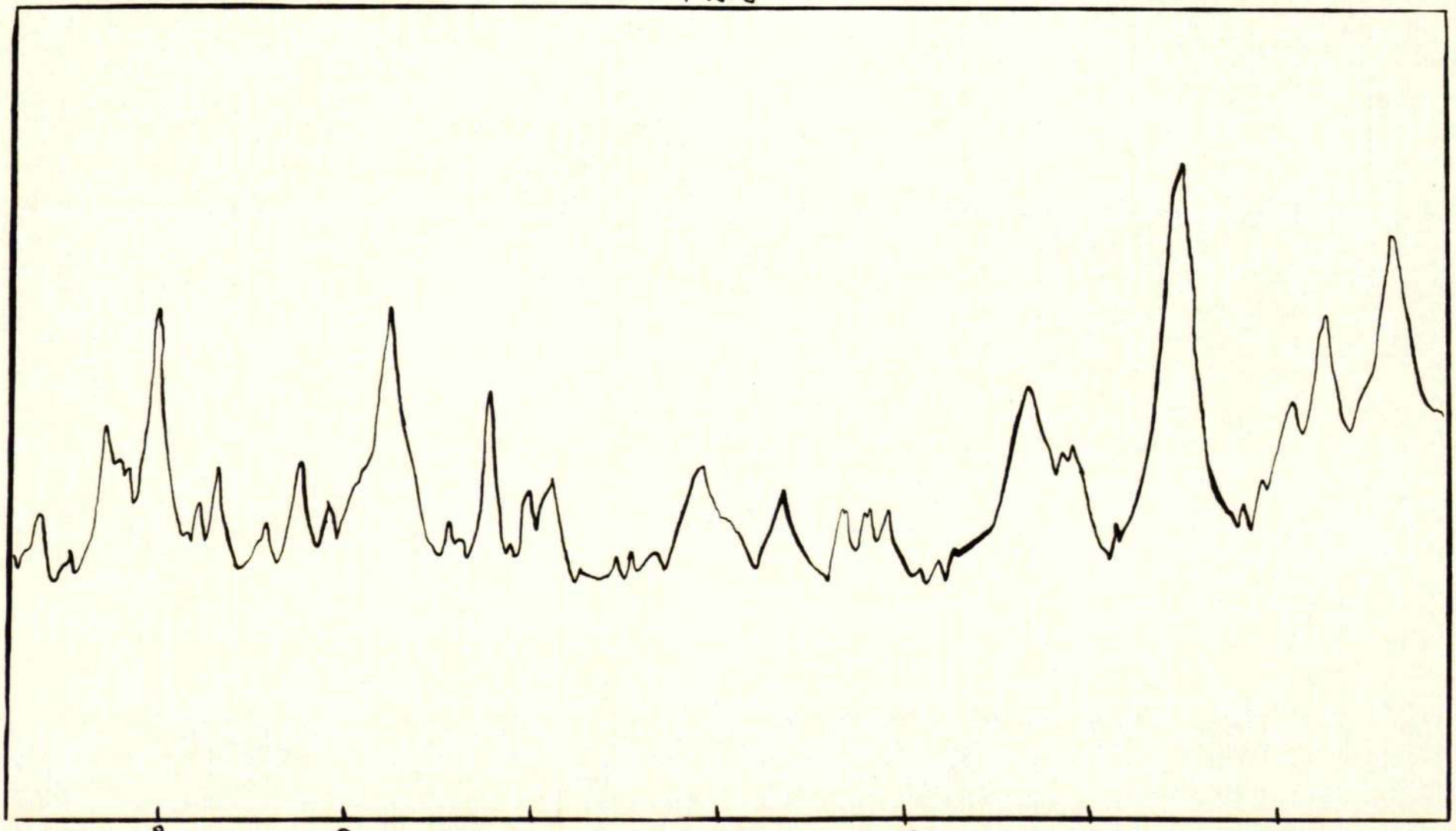
No other chloro-isomer present - showed by paper

chromatography of an unrecrystallised 2:4 DNP sample from fract.(ii). No VPC was carried out on pyrolysis 4.

Pyrolysis 5 was subjected to full analysis by VPC and IR means.

Column	30% Silicone E301 on Celite	30% Silicone E301 on Celite	30% Silicone E301 on Celite (new column)
Temp.°	168°	120°	168°
N_2 flow	1.2 l./hr.	1.2 l./hr	1.2 l./hr
Inlet press.	536 mm.	540 mm.	540 mm.
Outlet press.	152 mm.	173 mm.	155 mm.
<u>Fraction (i)</u> Retention times(min.)	1.6 (trace) 3.4 5.1 8.0 10.0 15.8 20.5	7.5 13.6 23.2(trace) 25.4 stopped	1.6(trace) 3.4 5.1 7.8(trace) 8.0 10.0 15.7 20.5
<u>Fraction (ii)</u> Retention times(min.)	3.5 8.0 9.9 15.7 20.4		
<u>Fraction (iii)</u> Retention times (min.)	15.7 20.4		

FIG. 8



Standards (min.)

Chlorobenzene	3.4	7.5	3.4
m-Chlorotoluene	5.1	-	5.1
Diketen	1.6	-	-
o-Chlorostyrene	7.8	24.2	7.8
m-Chlorostyrene	8.0	25.4	8.0
p-Chlorostyrene	8.0	25.4	8.0
o-Chloroacetophenone	13.5	-	-
m-Chloroacetophenone	15.8	-	15.6
p-Chloroacetophenone	15.5	-	-
m-Chlorobenzaldehyde	9.9	-	10.0
Vinyl m-chlorobenzoate	20.5	-	20.5

The following compounds are therefore present: chlorobenzene, m-chlorostyrene, o-chlorostyrene, m-chlorobenzaldehyde, m-chloroacetophenone, m-chlorotoluene, vinyl m-chlorobenzoate.

There is a very minor peak, too small to really define, which corresponds to diketen. The presence of o-chlorostyrene is supported by IR results (see Fig.9). Very small peaks at 1042, 770, 1132, 1095 cm^{-1} indicative of o-chlorostyrene (standard) are present in the IR spectrum of fract.(i). There are also very faint peaks at 1090, 1018, and 833 cm^{-1} which correspond to the standard p-chlorostyrene. The main

product, however, is m-chlorostyrene.

A positive anhydride test was obtained (Davidson - Newman).

An IR of the gas shows the presence of small quantities of methane, ethylene and acetylene.

Pyrolyses 6 and 7

On each run the 2:4 DNP(a)/2N-HCl trap gave an orange precipitate: on recrystallisation m.p. 159°. Mixed m.p. acetaldehyde derivative 160°. Paper chromatography showed presence of only one peak.

Cold trap: positive water test ($CuSO_4$).

Pyrolysis 6 yielded 2.0g. solid and 18.0g. liquid. Solid recrystallised from water: p-chlorobenzoic acid (m.p. and mixed m.p. 234°). The acid amide was prepared, m.p. 177° [lit. 179°].

The liquid was fractionated.

(i)	25-50°/12mm.	- 1.5g.
(ii)	50-110°/12mm.	- 10.0g.
(iii)	110-140°/12mm.	- 4.0g.
Residue	> 140°/12mm.	- 2.8g.

Fract.(ii) p-chloroacetophenone confirmed by 2:4 DNP (m.p. and mixed m.p. 231°). A sample of the 2:4 DNP obtained from fract.(ii) and subjected to paper chromatography without prior recrystallisation, showed the presence of only p-chloroacetophenone. Only vinyl p-chlorobenzoate and p-chloroacetophenone were detected (infra-red) in fract.(ii), though VPC showed

the presence of traces of other compounds. VPC gave the following results (Pyrolysis 7 unfractionated).

Column	30% Silicone E301 on Celite	10% Silicone E301 on Celite
Temp.°	162°	134°
N_2 flow	1.2 l./hr.	1.8 l./hr.
Inlet press.	518 mm.	430 mm.
Outlet press.	162 mm.	230 mm.
	Retention times (min.) Pyrolysis 6	Retention times (min.) Pyrolysis 7
Fract. (i)	3.3 (minor) 5.5 (minor) 9.0 (minor) 11.5 18.5 22.5	4.0 7.7 13.1 15.5 19.9 38.0 53.0
Fract. (iii)	18.4 22.4	
Standards		
Chlorobenzene	3.3	4.0
p-Chlorotoluene	5.5	13.1
p-Chlorostyrene	8.9	15.4
p-Chlorobenzaldehyde	11.5	19.8
p-Chloroacetophenone	18.4	38.0
Vinyl p-chlorobenzoate	22.5	52.5

Products present are therefore: chlorobenzene, p-chloroacetophenone, p-chlorostyrene (no trace o-isomer by VPC), vinyl p-chlorobenzoate, p-chlorobenzaldehyde and p-chlorotoluene.

The residue was mainly p-chlorobenzoic acid (m.p. and mixed m.p. 235°).

An IR spectrum of part of fract.(i) (refractionated) shows a very minor peak at 1132 cm^{-1} and also one at 1042 cm^{-1}, both of which are characteristic of o-substitution in the benzene ring and also occur in the IR of a standard o-chlorostyrene. There is therefore the possibility that o-chlorostyrene is present. The main fraction however is the p-isomer (IR and VPC methods).

A positive anhydride test was obtained.

Pyrolysis 8

The 2:4 DNP(a)/2N-HCl trap gave an orange precipitate: on recrystallisation m.p. 159°. Mixed m.p. acetaldehyde derivative 159°.

No fractionation was carried out: mixture analysed by VPC.

Column	10% Apiezon "L" on Celite
Temp.°	169°
N_2 flow	1.3 l./hr.
Inlet press.	565 mm.
Outlet press.	185 mm.

Pyrolysate Retention times (min.)	Standards	Retention times (min.)
1.2		
1.6	Benzene	1.6
1.9	Toluene	1.9
3.4	Styrene	3.4
4.0	Benzaldehyde	4.6
7.5	Acetophenone	7.5
10.0	Vinyl benzoate	10.0
13.5	Benzoic acid	13.5

There was no trace of benzaldehyde or keten. Compounds found to be present were: benzene, toluene, styrene, acetophenone, vinyl benzoate.

A positive anhydride test was obtained.

Pyrolysis 9

The pyrolysate containing 15.0g. was divided into two fractions, 3.0g. solid and 12.0g. liquid. The solid was found to be benzoic acid, m.p. 120°. Mixed m.p. benzoic acid 120-121°. Benzoic acid was confirmed by IR spectrum.

The liquid was fractionated to give:

Fract.	(i)	20-60°/4mm.	0.5g.
	(ii)	60-90°/4mm.	6.25g.
	(iii)	90°-115°/4mm.	4.4g.
	Residue	> 115°/4mm.	0.8g.

The residue was a mixture of benzoic acid and tars. The three fractions were analysed by VPC.

Column	10% Apiezon "L" on Celite.	10% Apiezon "L" on Celite
Temp.°	80°	162°
N_2 flow	1.4 l/hr.	1.4 l/hr.
Inlet press.	412 mm.	514 mm.
Outlet press.	105 mm.	155 mm.
	Retention times (min.)	Retention times (min.)
Fract. (i)	3.5(trace) 8.0 12.4 19.6	
Diallyl ether	3.5	
Benzene	8.0	
Toluene	12.3	
Allylbenzene	19.6	
Fract. (ii)		1.8 2.1 3.0 4.5(trace) 6.0(trace) 7.1
Fract. (iii)		2.1 7.1 13.0
Allyl benzene		1.8
Benzaldehyde		2.1
Propiophenone		4.5
Allyl benzoate		7.1
Benzoic acid		13.0

Allylbenzene, diallyl ether, toluene, benzaldehyde, and propiophenone were present (VPC) in the non-gaseous pyrolysate. Two peaks accounting for ca. 0.5% remained unidentified.

The gaseous pyrolysate contained hex-1-ene [IR bands at 3080, 2960, 1820, 1647, 1456, 998, 914, and 738 cm^{-1}] methylacetylene [3380, 2160, 1269, 1244, 1460 and 1440 cm^{-1}], ethylene [950 cm^{-1}] and methane [1300 cm^{-1}].

The cold trap contained hex-1-ene, methylacetylene, ethylene, methane and (after evaporation) water and acrolein [2985, 1690, 1418, 1355, and 1240 cm^{-1}].

Pyrolysis 10

The pyrolysate was fractioned to give:

(i)	20-40°/17mm.	2g.
(ii)	80-130°/17mm.	1g.
(iii)	130-150°/10mm.	5.5g.
Residue	> 150°/10mm.	6.5g.

Fract.(iii) was further fractionated to give 2.5g. solid and 3.0g. liquid. The solid was recrystallised from hot water: o-chlorobenzoic acid (m.p. and mixed m.p. 138°). The liquid fraction gave a positive anhydride test.

Fract.(i) gave an IR spectrum identical to that of chlorobenzene.

The residue was extracted with sod. carbonate and the extract acidified. 3.0g. white solid obtained. Recrystallised from water: o-chlorobenzoic acid (m.p. and mixed m.p. 138°). The remainder of the residue consisted of tarry and charred material.

VPC showed fract.(i) to contain chlorobenzene and traces of diallyl ether and o-allylchlorobenzene.

Column.	10% Apiezon "L" on Celite
Temp.°	160°
N_2 flow	1.6 l./hr.
Inlet press.	520 mm.
Outlet press.	135 mm.

Fract.(ii) gave peaks with retention times 1.5, 2.5, 3.4, 4.8, 11.5 and 17.4 min. These corresponded to standards: chlorobenzene 1.5, o-chlorotoluene 2.5, o-allylchlorobenzene 3.5, o-chlorobenzaldehyde 4.8, and allyl o-chlorobenzoate 17.4 min.

Fract.(iii) (after filtration) contained almost exclusively starting material and was of a reddish colour.

The IR spectrum of the gas was almost identical with that of allyl benzoate. Similarly, the cold trap, after evaporation of the more volatile components, showed the presence of acrolein (ca. 0.2g.).

Pyrolyses 11 and 12

The pyrolysate from pyrolysis 11 was chromatographed.

Column	30% Silicone E301 on Celite
Temp.°	168°
Gas flow	1.2 l./hr.
Inlet press.	540 mm.
Outlet press.	155 mm.

Peaks were obtained at 3.4, 5.1 and 15.3 min., corresponding to chlorobenzene, p-chlorotoluene and p-chloroacetophenone.

Pyrolysis 12: the pyrolysate was fractionated to give 0.7g. material with a boiling range 20-90°/3mm.(fract.(i)) and a remainder boiling above this temperature. Fract.(i) was chromatographed on the "Pye Argon" machine.

Temp.° = 150°

Flow rate = 12 ml./min.

Column 10.01% Apiezon "L" on Celite

Fract.(i) gave peaks at 1.9, 3.4, 10.6, and 16 min.

Standards:

chlorobenzene	1.9 min.
p-chlorotoluene	3.4 min.
p-chlorobenzaldehyde	10.6 min.
p-chloroacetophenone	16.0 min.

There were no other peaks and the remainder was pure unchanged starting material with a trace of p-chlorobenzaldehyde.

An IR of the gas showed the presence of carbon monoxide ethylene and methane.

Pyrolysis 13

A solid fraction was filtered from the pyrolysate and recrystallised from alcohol/water: trans-stilbene (m.p. and mixed m.p. 123°). VPC confirmed presence of only one compound.

The remainder was fractionated to give:

(i)	18-50°/1mm.	0.5g.
(ii)	50-140°/1mm.	3.5g.
(iii)	140-230°/1mm.	8.5g.
	Brown tarry residue	6.0g.

Fract.(iii) was further divided to give 3.0g. solid and 5.5g. liquid: solid recrystallised from alcohol/water: trans-stilbene (m.p. and mixed m.p. 123°; dibromo derivative m.p. 238°, lit. 239°).

Fract.(i),(ii), and the remainder of fract.(iii) were chromatographed.

Column	20% Silicone oil on Celite
Temp.°	108°
N_2 flow	2.4 l./hr.
Inlet press.	578 mm.
Outlet press.	177 mm.

Fract.(i); Peaks at 2.2, 3.7, 4.4, 6.5, and 7.8 min.(trace).

Standards:	Benzene	0.95 min.
	Toluene	2.2 min.
	Phenylacetylene	4.4 min.
	Phenol	6.5 min.

Two peaks (both small) remained unidentified.

Column	20% Silicone on Celite
Temp.°	193°
N_2 flow	2.4 l./hr.
Inlet press.	578 mm.
Outlet press.	177 mm.

Fract.(ii); Peaks at 1.2, 2.6, 5.6, and 14.5 min.

Standards:		
	Phenol	1.2 min.
	trans-Stilbene	14.4 min.

Fract.(iii); Peaks at 1.2, 2.6, 5.0, 5.7, 7.8, 9.9, 14.4, 18.8, and 23.8 min.

Standards:		
	Phenol	1.2 min.
	Diphenyl	5.0 min.
	Dibenzyl	7.8 min.
	trans-Stilbene	14.4 min.
	Anthracene	18.9 min.
	Phenyl cinnamate	23.8 min.

Thus three minor compounds remained unidentified, all fairly high boiling compounds.

Pyrolysis 14

No trace of any aldehyde or ketone was obtained in the 2:4 DNP(a) trap. The mixture was chromatographed and only one peak, corresponding to phenol, was obtained. No trace of any original starting material or benzene could be detected.

Pyrolysis 15

The pyrolysand was chromatographed without fractionation.

Column	20% Silicone on Celite
Temp.°	206°
N_2 flow	2.5 l./hr.
Inlet press.	630 mm.
Outlet press.	195 mm.

Two peaks were obtained at 5.5 and 10.0 min. They corresponded to dibenzyl and trans-stilbene respectively.

IR spectra of trans-stilbene and dibenzyl are very similar apart from a major peak at 905 cm.$^{-1}$ present in dibenzyl which is absent in trans-stilbene and the presence of a strong peak at 970 cm^{-1} in trans-stilbene [trans-CH=CH.] which is absent in dibenzyl.

An IR spectrogram of the trans-stilbene pyrolysate gives a spectrum identical to that of trans-stilbene with the addition of a marked peak at 905 cm.$^{-1}$, characteristic of dibenzyl. No other breakdown products were detected.

Pyrolysis 16

A slight cloudiness was noticed in the 2:4 DNP(a)/2N.HCl trap but the derivative was too minute in amount for identification. The pyrolysate was extracted with acetone and chromatographed on the "Pye Argon" machine.

Column	10.01% Apiezon "L" on Celite		
Gas flow	15 ml./min.	Temp.	150°

Peak at 3.0 min, corresponds to benzaldehyde. No other peaks were obtained.

The solid pyrolysate was recrystallised from hot water. White crystals m.p. 121° were obtained. Mixed m.p. benzoic acid 121°.

The gas sample contained only propene, but a slight peak at 1724 $cm.^{-1}$ was indicative of acetone [C = O group].

The cold trap, containing 3.0g. liquid, proved to be propene (b.p. - 47°). Confirmed from IR [2950, 1832, 1815, 1656, 1629, 1468, 1399, 990, and 910 $cm.^{-1}$].

PART II

14. Onset Temperature

14.1. Introduction

From the work shown in Part I of this thesis, it can be seen that the majority of ester breakdowns occur by two or more competing routes. In an attempt to determine the onset (or threshold) temperature of each reaction (i.e. the temperature at which each makes its first appearance) an apparatus similar to that devised by Mackinnon[89] has been used. Whilst the absolute significance of any particular onset temperature had not been established, the method provided an adequate comparison of the stabilities towards heat of various esters. The apparatus (described later) proved both simple to operate and reproducible ($\pm$ 5°).

With a knowledge of the onset temperatures of the various scissions in different compounds it might be possible, by the incorporation of molecules with high onset temperatures, to increase the thermal stability of certain polymers, e.g. a copolyester of the type $\sim CH_2.CH_2O_2C(CH_2)_nCO_2.CH_2.CH_2\sim$ could perhaps be stabilised somewhat by either increasing or decreasing n.

14.2. Related Work

Little similar work is recorded in the literature: a brief summary is given below.

In 1932, Norris[90] studied systematically the pyrolysis of hydrocarbon chains. He found that, although the carbon - to - carbon linkages in paraffin hydrocarbons are assumed to have the same heat of formation, the temperatures at which the several bonds broke were different. By regulating the temperature, he could also break the bonds successively, and thus, from the products of pyrolysis, find the order in which the bonds yielded to the influence of heat. From this he reached two conclusions.

(a) different bonds break at different temperatures

(b) the structure of the molecule has a marked effect on the temperature of breakdown - the larger the hydrocarbon chain, the lower the cracking temperature.

Later work by Norris and Cresswell[91] showed that when the members of a homologous series were heated under fixed conditions, the temperature at which each compound first showed signs of decomposition at a particular bond varied with the nature of the radical present. In the pyrolysis of alkyl triphenylacetates the products formed on pyrolysis were triphenylmethane, carbon dioxide and carbon monoxide, and an olefin. These products probably occurred *via* a primary A^1 scission to acid and olefin followed by secondary decarboxylation of the acid.

x glass or quartz.

In determining the "cracking" temperature, the esters were heated in tubes sealed to a mercury manometer and evacuated. Alkyl esters of the series $CPh_3.CO_2.R$ gave the following results.

R	Temp.°	R	Temp.°	R	Temp.°
CH_3 ..	195°	C_3H_7 ..	170°	C_4H_9 ..	183°
C_2H_5 ..	188°	iso C_3H_7 ..	155°	iso C_4H_9 ..	149°
				s-C_4H_9 ..	164°

Isobutyl triphenylacetate was found to crack in vacuum at 149°. When heated in an evacuated tube for 18 hr. at 140°, 8 hr. at 145°, and 1 hr. at 147°, it was found that no breakdown occurred. However, on raising the temperature to 149°, breakdown was noted within one hour. These results show that for a specific mode of breakdown in any given ester, the "cracking" temperature has a definite significance.

It is interesting to note here that, as expected, the methyl ester has the highest onset temp.: also, that the two esters containing an α-branched alkyl group have the lowest cracking temp.

In 1943, Petit[92] found that the order of thermal cleavage of the different bonds in an organic compound varied with the experimental conditions. These variations in stability were explained by assuming the existence of two antagonistic forces. The first, a steric factor, depended on the increasing number of carbon atoms and tended to increase stability (contrast the results of Norris[90,91]:

the second, a polar factor, tended to decrease the stability.

Alvara[93] evolved a relationship between the onset temperature of decomposition and the activation energy. He stated that the onset temperature T, for decomposition of a compound could be expressed as $T = Ea/\Delta Sa$, where Ea is the energy of activation and $\Delta Sa = R \ln B$ (B = the coefficient in the Arrhenius equation). He applied this formula to three explosive substances and the results were shown to agree satisfactorily with published data.

Smith and Wetzel[57] studied the effect of molecular size on the ease of pyrolysis of esters. They found that esters of high molecular weight decomposed at a lower temperature than their lower homologues. Obrimov[94] has stated similar results; and stearates and palmitates[95] are reported to undergo pyrolysis at lower temperatures than acetates. However, as the molecular size increased stepwise by a series of methylene groups, the decomposition temperature decreased in a zig-zag or alternating rather than a regular fashion. The results for a homologous series of cyclohexyl esters illustrate this:-

Formate 490°: acetate 496°: propionate 485°:
butanoate 490°: pentanoate 479°; hexanoate 484°:
heptanoate 473°: octanoate 478°: nonanoate 471°:
decanoate 478°: octadecanoate 460°:

This type of temperature is described as the "characteristi temperature", i.e. the temperature at which, for each pyrolysand the plot of percentage yield/pyrolysis temperature vs. pyrolysis temperature shows a maximum. In effect it is the temperature at which pyrolysis is the most efficient.

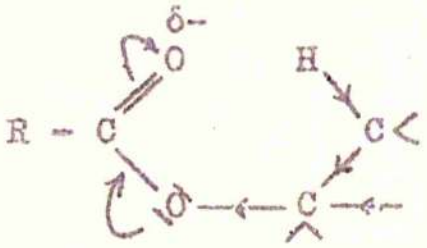
Smith and Wetzel[57] also found that substituted cyclohexyl benzoate with electrophilic groups in the o- and p- positions pyrolysed more readily than cyclohexyl benzoate itself (cf. pyrolysis of vinyl o-, m-, and p-chlorobenzoate and vinyl benzoate: section 3.4.4.). Further results showed that the temperature of pyrolysis was directly related to the strength of the acid from which the ester was prepared, and to the C-O stretching bond in the infra-red spectra of the esters.

Bailey and Hewitt[105] found that the extent of pyrolysis was directly related to the pK_a of the corresponding acid.

Smith and Wetzel[57] had not shown whether the decreasing pyrolysis temperature was due to a change in the size of the acyl portion alone, or to a change in the total molecular weight of the ester. To settle the point, Smith and Bagley[96] pyrolysed nine isomeric aliphatic esters, each of molecular weight 200 and formula $C_m H_{2n+1} CO_2 C_n H_{2m+1}$ $(n + m = 12)$, and showed that ease of pyrolysis is here a function of the total molecular weight of the ester, and not of the acyl portion alone. All nine esters showed a characteristic temperature within the very narrow range 558 - 62 ± 1°.

Maccoll[35] has shown that α-methyl substitution in the

alkyl grouping of an ester leads to an increase in the rate of pyrolysis. The orthodox Hurd and Blunck transition state can be written thus:



Here the α-methyl substituent tends to stabilise the ring. Hence tertiary esters would be expected to undergo pyrolysis at lower temperatures than secondary, and secondary at lower temperatures than primary. This is confirmed by the following results.[35]

Relative rates of gas-phase elimination

	Ethyl	Isopropyl	t-Butyl
Formate	1	20	720
Acetate	1	26	515

DePuy[38] has determined the relative rates of pyrolysis of various s-butyl compounds as follows:

s-Butyl compound	Relative rate
Acetamide	0.04
Acetate	1.0
Vinyl ether	1.3
Trifluoroacetate	10.0

From these results he deduces that the rate of pyrolytic elimination is roughly proportional to the change in bond energies involved in the reaction:

The most general change in properties in the thermal decomposition of organic molecules is an increase in the vapour pressure of the system brought about by cleavage of the molecule into smaller more volatile fragments. Blake[97] has defined the decomposition point as the temperature (T° Fahr.) at which $dp/dt = 0.016$ mm. Hg./sec. or 50.4 mm. Hg./hr. He has also derived an equation, using this decomposition temperature, whereby it is possible to evaluate the frequency factor A, and hence the activation energy E of the reaction:

$$A = \frac{Vg A^{1}}{V_B n_B^{V} \, b \, R \, T_D^{1}}$$

where $A = 10^{-6} A^{1}$

Vg = vol. of gas phase. V_B = vol. of liquid phase

n_B = mol conc. of compound

V = order of reaction

b = no. of mols.(gaseous) formed/mol. thermally decomposed

R = molar gas constant

T_D^1 = decomposition temp. (°C)

The decomposition points of a series of compounds are the temperatures at which all have the same isothermal rates of pressure rise. Decomposition points therefore give precise comparisons of thermal stabilities, analogous to the use of boiling points for comparing volatility. Typical temperatures obtained by Blake are:-

Compound	T_D^1	E(k.cal)
2-Ethylhexyl sebacate	275°	53.1
Octyl sebacate	278°	52.0
Benzyl sebacate	296°	67.0
Phenyl sebacate	280°	ca. 46.0
Octyl phthalate	265°	52.4
Octyl isophthalate	270°	40.5
Octyl terephthalate	272°	52.6

It is interesting that McCall and Rawlings[98], using similar techniques, obtained a decomposition temperature (290°) for 2-ethylhexyl sebacate. This variation in the results of different workers, using similar systems, has

a parallel in the present work. The onset temperatures recorded by Mackinnon[89] for various esters could not at first be duplicated, within reasonable experimental error, by other workers in this laboratory using similar apparatus and apparently the same technique. Subsequently, the present writer refined and standardised the apparatus and technique; reproducible results are now accessible, of apparently absolute significance.

14.3. General Discussion

As an organic compound is raised to higher and higher temperature, the vibrational energy distributed among the bonds of the molecule increases. In the simple case of a diatomic molecule, when vibrational energy becomes equal to bond strength, the molecule will rupture, and the energy of activation of decomposition will equal the bond strength. In more complex molecules, the strength of the weakest bond will determine the thermal stability. However, most molecules can decompose with activation energies lower than the bond energies of their weakest bond[97], owing to formation of a transition state in which bonds are broken and formed simultaneously. An example of this is the pyrolysis of esters. No bond energy in an ester is significantly weaker than in a paraffin: yet

2-ethylhexyl sebacate has a decomposition temperature 70° lower than octacosane, $CH_3(CH_2)_{26}CH_3$.[97] The activation energy for A^1 scission is ca. 53 k.cal. which is much less than the 83 k.cal. required for direct scission of the C-O bond. When this low energy path is blocked by replacement of the β-hydrogen atom, the decomposition point can be raised by as much as 45°[97] (1-methylcyclohexylmethyl sebacate) and the activation energy is increased to 58 k.cals.

When a compound (A) decomposes into one or more molecules of decomposition product, the rate of disappearance of A will be dn_A/dt, and this can be given by

$$dn_A/dt = -k\, n_A^V$$

where k = rate constant

n_A = conc. of starting material

V = order of reaction.

However, the rate constant k can also vary with temperature according to the Arrhenius rate law:

$$k = Ae^{-E/RT}$$

Now, for any given decomposition, A and E will be constant[100] and the rate will depend solely on temperature T. The decomposition will therefore proceed continuously, but at temperatures below the "decomposition" or onset temperature,

the rate will be so slow that the products of pyrolysis cannot be detected by the apparatus used (described later). From the above equation, it can also be seen that the higher the activation energy the lower will be the velocity of the reaction at any given temperature. Now, as the temperature is increased, the vibrational energy distributed among the bonds will increase to a point where it equals the bond strength and the bond ruptures. The temperature at which this energy relationship is reached will then be the onset temperature and correspond to an increase in rate of the decomposition, such that the products can be readily detected by the apparatus.

So long, therefore, as the detection system remains the same, and is sufficiently insensitive to justify neglect of the slow decomposition at lower temperatures, the onset temperature will be reproducible and represent the temperature at which bond rupture starts at an increasing pace.

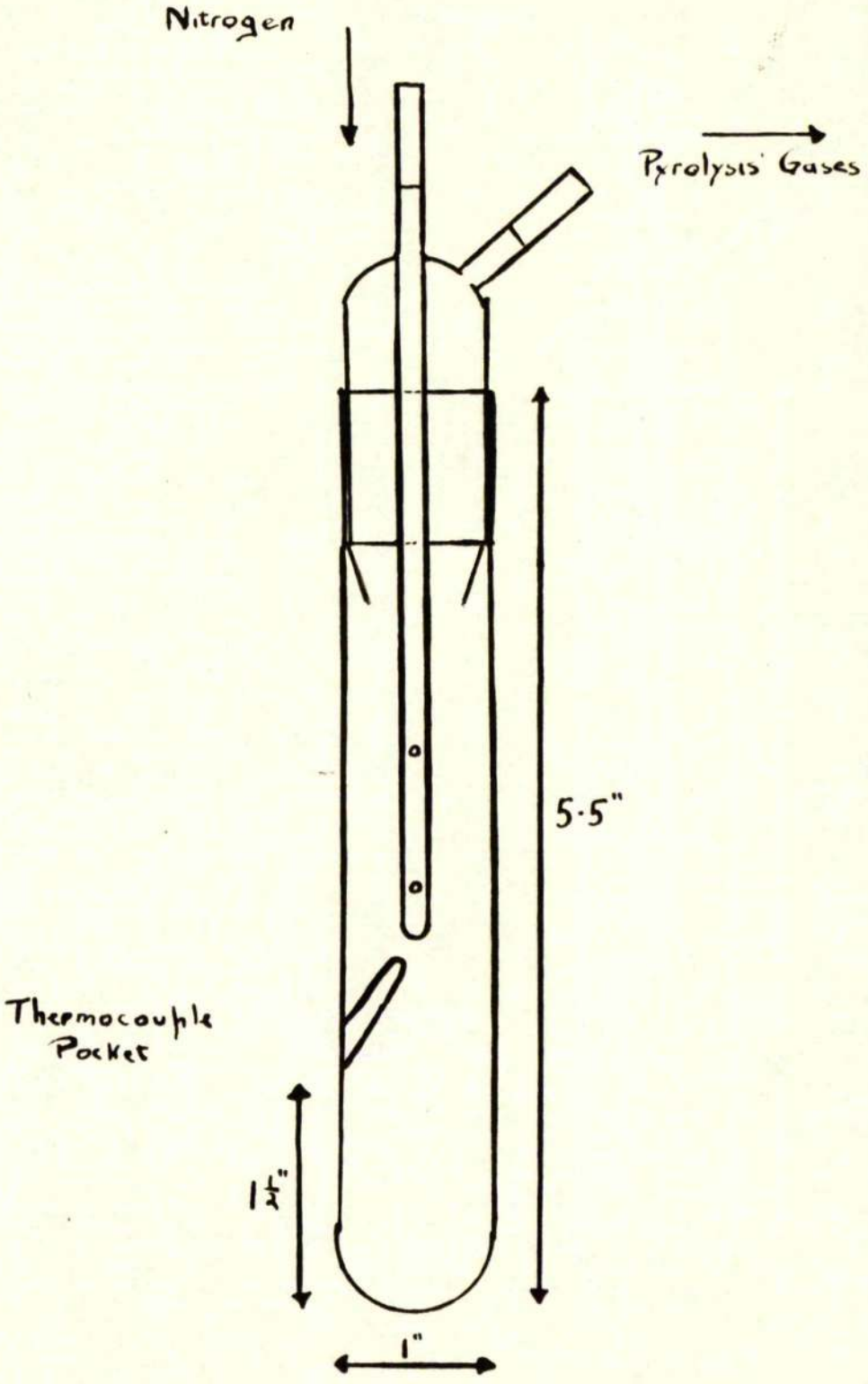


FIG. 10

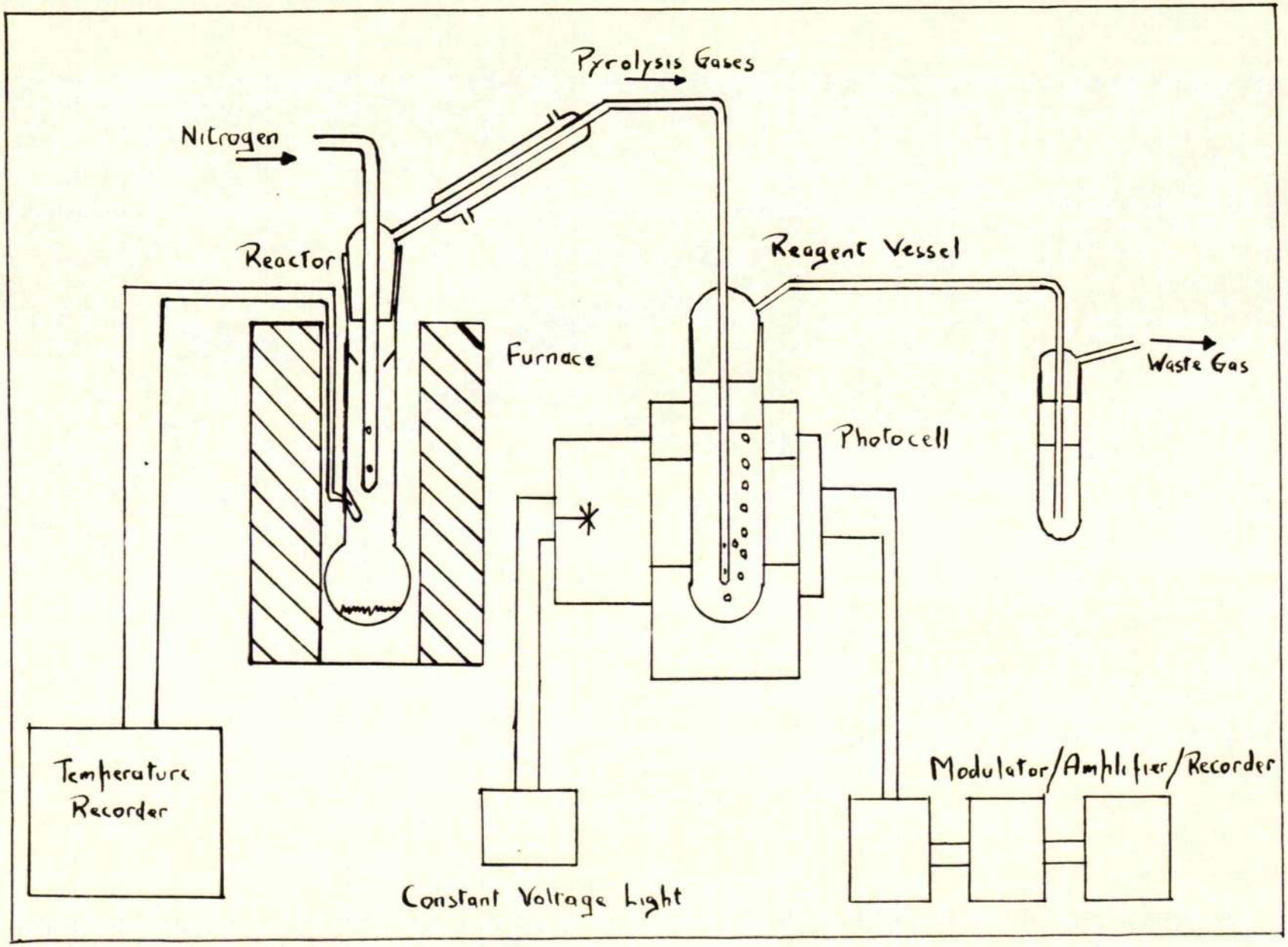

Pyrolysis Gases
Nitrogen
Reactor
Reagent Vessel
Furnace
Waste Gas
Photocell
Temperature Recorder
Modulator/Amplifier/Recorder
Constant Voltage Light

FIG. 9

15.1. Apparatus

The original apparatus was devised and deacribed by Mackinnon.[89] Since then, several modifications have been made, but the basic principle remains the same. The modified apparatus is as illustrated in Fig. 9.

A small sample of the pyrolysand (ca. 1.0g.) is placed in the reactor (Fig. 10): the temperature is raised at a rate of 1°/min. and continuously recorded by a directly calibrated Honeywell-Brown recorder. The thermocouple, placed in a small pocket of the reactor, is designed so as to avoid fluctuation due to flow of condensing pyrolysand down the walls of the tube. (A modified reactor, designed later to prevent liquid and vapour from coming into direct contact in the reaction zone, gave exactly the same results as the original). Volatile products are carried from the reactor by a slow stream of dry oxygen-free nitrogen and pass through an optical cell placed between a constant voltage light source and a sensitive photoelectric cell. The optical cell contains a reagent giving either a colour reaction or a turbidity (due to formation of a precipitate) specific to the volatile component being studied. When breakdown occurs in the pyrolysand, the output of the light cell is immediately altered and this is recorded

on a chart connected to a Pye amplifier/galvanometer. The reading on the temperature recorder corresponding to the initial deviation caused by a variation in light absorption in the optical cell is then taken as the onset temperature for that particular reaction.

The reagents used in the optical cell were :-

	Scission	Volatile component	Reagent
1.	A^1	olefin	Br_2/CCl_4
2.	A^2	acetylene	$AgNO_3$/ethanol
3.	B^2	aldehyde or ketone	2:4 DNP/2N HCl
4.	C^1	carbon monoxide	Phosphomolybdic acid/$PdCl_2$
5.	C^2	carbon dioxide	Sat. $Ca(OH)_2$

1. A solution of ca. 0.1% Br_2 in carbon tetrachloride giving the colour change: orange --> colourless.

2. An acetylene reagent was made up by adding 25 ml. 10% Ag NO_3 to 70 ml. ethanol. A white precipitate was obtained on addition of acetylene due to the formation of a silver acetylide

$$CH \equiv CH + Ag\ NO_3 \longrightarrow HC \equiv C.Ag.AgNO_3 + HNO_3$$

3. A saturated solution of 2:4-dinitrophenylhydrazine in 2N-HCl was used. On addition of aldehyde or ketone a yellow or red precipitate of 2:4-dinitrophenylhydrazone was formed.

4. An acidified solution of phosphomolybdic acid and palladium turns blue in the presence of a reducing agent (CO). The CO is adsorbed and activated to bring about the reaction

$$2\ MoO_3 + CO \longrightarrow Mo_2O_5\ (\text{blue}) + CO_2$$

5. A cold saturated solution of calcium hydroxide gives calcium carbonate (white ppte.) on addition of CO_2.

15.2. Purpose of this work

The aim of this work was to examine a series of homologous compounds and to study the onset temperatures of two competing reactions. In addition, the relative stabilities of various other compounds were compared and an attempt made to relate them to various physical properties of the molecules.

Another investigation concerned the possibility of isolating and studying kinetically one particular mode of scission by operating just above its specific onset temperature but below the onset temperatures of any other competing reactions.

16. Onset Temperatures of Esters type $R.O_2C(CH_2)_n.CO_2.R$

16.1. R = Et, n = 1 - 8 and n = 12. A^1 type scission

The first homologous series studied consisted of esters of the type $Et.O_2C(CH_2)_n.CO_2Et$, n = 1 - 8 and n = 12. The onset temperature of alkyl-oxygen scission for each ester was obtained: the products of this route being the corresponding acid and ethylene.

The apparatus was as described in Section 15.1, the optical cells containing a solution of Br_2/CCl_4.

The onset temperatures [$T(CH_2:CH_2)$] of A^1 scission were found to be as below:

Ethyl Ester	n	$T(CH_2:CH_2)$
oxalate	0	300°
malonate	1	320°
succinate	2	383°
gluterate	3	360°
adipate	4	333°
pimelate	5	370°
suberate	6	383°
azelate	7	350°
sebacate	8	360°
tetradecan-1,12-dioate	12	375°

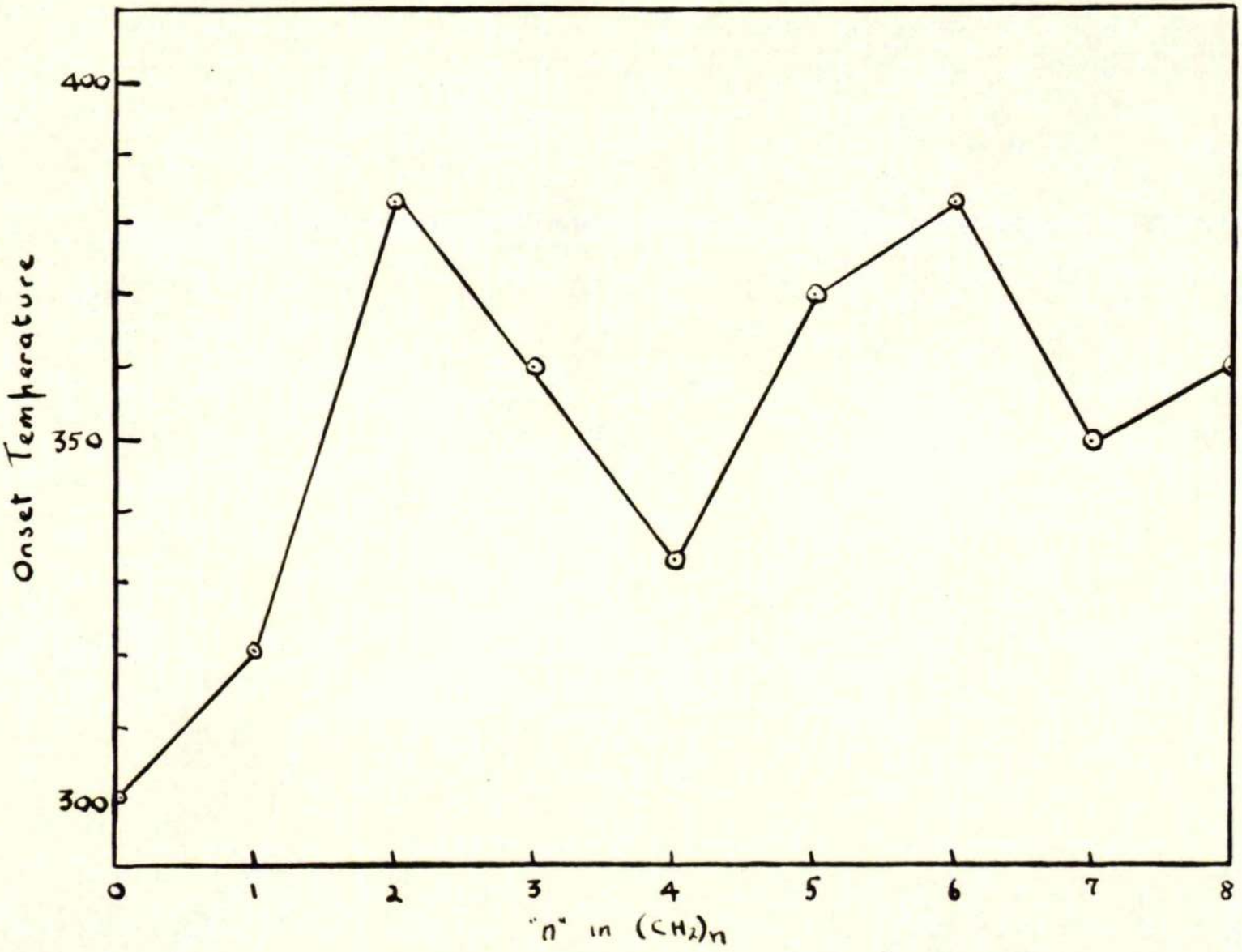


FIG. 11 $T(CH_2=CH_2)$ OF $EtCO_2(CH_2)_nCO_2Et$

From the graph in Fig.11 it can be seen that maximae occur corresponding to values of $\underline{n} = 2$ and $\underline{n} = 6$ and that a minimum occurs at a value of $\underline{n} = 4$. Neglecting the onset temperature of the adipate, it becomes obvious that the values obtained tend to follow a zig-zag pattern as found by Smith and Wetzel[57] for A^1 scission of the cyclohexyl esters of the series $RO_2C(CH_2)_n.CH_3$, with odd numbered members having lower onset temperatures than even numbered members. However, there is no general decrease in onset temperatures as $\underline{n}$ increases, as these workers found for their "characteristic" temperatures: rather there is a levelling off towards a final onset temperature in the region 350° - 370°, as $\underline{n}$ increases.

An attempt to obtain some correlation between physical properties of the esters and the observed onset temperatures was now made. No single property proved entirely satisfactory in explaining the results but several showed some interesting comparisons.

No connection between the onset temperatures and boiling points of the compounds could be found: this is as expected, as, in the pyrolysis of esters, bonds are broken and formed, whereas the boiling points depend on the breaking of intermolecular forces. However, it is interesting to note that a similar alternation is found

in the melting points of various esters of dicarboxylic acids, e.g. the alternation is very marked for the t-butyl esters.[101]

Various physical constants of the diethyl esters were then examined and from some of these it was obvious that diethyl succinate behaved in an anomalous manner.

Ethyl Ester	Molar Refractivity[102] $\mu \times 10^{18}(25°)$	Viscosity[103] $\eta \times 10^{6}$ mol.vol.
oxalate	2.49	128.5
malonate	2.54	123.2
succinate	2.14	142.9
glutarate	2.41	132.0
adipate	2.40	137.9
pimelate	-	150.7
suberate	-	172.6
sebacate	2.49	188.6

Though the succinate exhibits anomalous behaviour, the adipate and suberate fall in line with the remainder of the series. No relationship between viscosity or refraction with onset temperature could be found.

Smith and Wetzel[57] found that the temperature of pyrolysis was directly related to the O-C stretching bond in the infra-red spectra of esters. This frequency in turn is a measure of the strength of the bond. Blake[97] has also found that there is a direct relationship between bond strength and decomposition temperature for a certain homologous series, though in his case the series had structure $C_6H_5 - M$, where M was a group $\overline{V}$ A metal.

A series of infra-red spectra of the compounds was therefore run and the wave number of the O-Et stretching bond for each ester established.[104] The bond in question is marked with an arrow.

$$-(CH_2)_n - \overset{O}{\overset{\|}{C}} - O \overset{\downarrow}{-} Et$$

Ethyl Ester	Wave No. (cm^{-1})
malonate	985
succinate	1005
glutarate	975
adipate	940
pimelate	965
suberate	975
azelate	967
sebacate	967

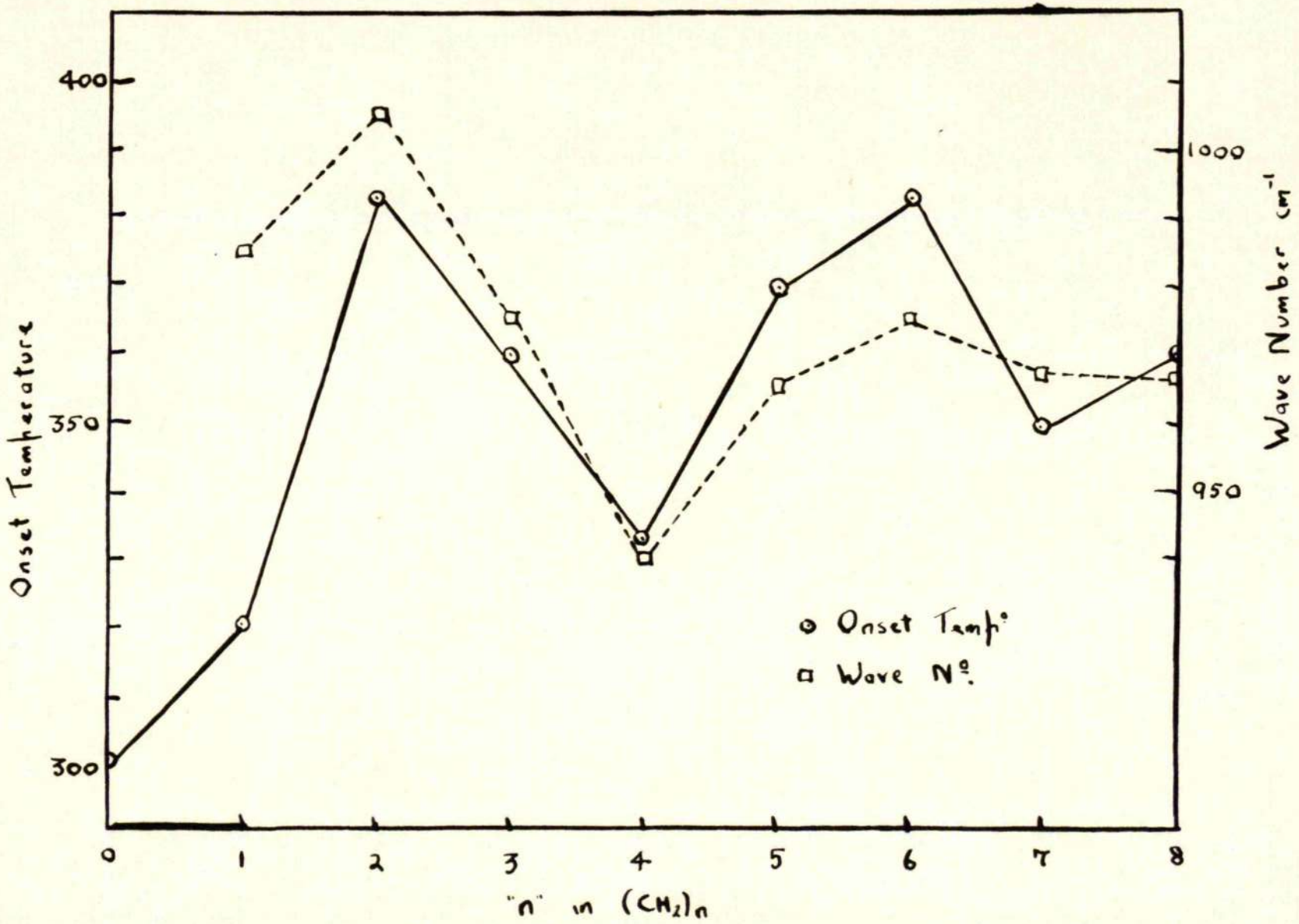
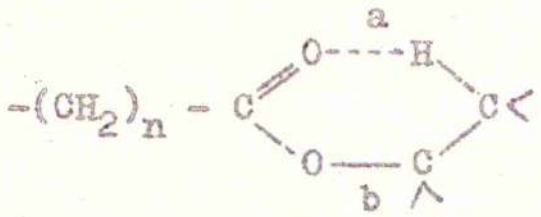

400
350
300
Onset Temperature
1000
950
Wave Number cm⁻¹
0
1
2
3
4
5
6
7
8
"n" in $(CH_2)_n$
o Onset Temp°
□ Wave No.

FIG. 12

From these figures it can be seen that there is a minimum at $\underline{n} = 4$ (adipate), a maximum at $\underline{n} = 2$ (succinate), and a smaller maximum at $\underline{n} = 6$ (suberate). Fig.12 shows that the pattern of the wave numbers conforms approximately to that of the onset temperatures of the ethyl esters. This suggests that the onset temperature is, at least to some extent, a function of the strength of the O-Et bond. This would be expected if the scission occurred <u>via</u> the Hurd and Blunck 6-membered ring, though it is not quite in line with the work of Maccoll[35], who suggested that the forming and not the breaking bond controlled the rate.



a = forming bond

b = breaking bond

No connection could be found between acid strength and onset temperature as suggested by Smith and Wetzel[57] and Bailey and Hewitt.[105] DePuy[38], however, has said that such a relationship does not exist: and the present results confirm this.

Acid	pK_{a1}	pK_{a2}
Oxalic	1.46	4.40
Malonic	2.80	5.85
Succinic	4.17	5.64
Glutaric	4.33	5.57
Adipic	4.43	5.52
Pimelic	4.47	5.52
Suberic	4.52	5.52
Azelaic	4.54	5.52
Sebacic	4.55	5.52

pK_{a_2} and pK_{a_1} refer to first and second stage ionisation constants.

A sample of diethyl 2:5-diphenyladipic acid had an onset temperature of 330° for A^1 scission; addition of two phenyl groups to the carbon backbone had therefore no effect on the mode of pyrolysis, causing no stabilisation of the transition stage with a consequent lowering of the onset temperature.

16.2. R = Pr^i, n = 1 - 8 and n = 12. A^1 type scission

The isopropyl esters of the same series of acids were pyrolysed and the onset temperatures obtained are as tabulated below. Products of pyrolysis were the corresponding acid and propene.

Isopropyl Ester	T(CH_2:CH.CH_3)
Malonate	265°
Succinate	300°
Glutarate	305°
Adipate	335°
Pimelate	330°
Suberate	337°
Azelate	340°

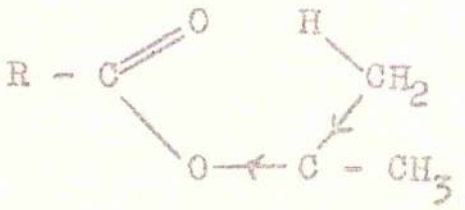
Isopropyl Ester	T(CH_2:CH.CH_3)
Sebacate	330°
Tetradecan-1:12-dioate	335°

In the A^1 scission of these isopropyl esters there are no distinctive maxima and minima, such as those shown by the corresponding ethyl esters. The onset temperatures are also generally lower. Apart from the first three esters in the series, all have onset temperatures within

the range 330 - 340°. This is ca. 20 - 30° lower than the ethyl esters. Hurd[28] had previously noted this effect for secondary esters, and Maccoll has stated that they pyrolyse faster than primary esters at the same temperature.

Apart from the first three members of the series, it appears that chain length and O-Pr^i bond strength have little effect on the onset temperature. The general pattern of breakdown is distinctly different from that of the primary esters, which suggests that some other factors not occurring in the breakdown of primary esters must be sought in the general mechanism of pyrolysis of these secondary esters. Two probable factors may be considered.

(a) Maccoll has stated that α-methyl substitution would tend to stabilise the transition state:



This may account for the decrease in onset temperature. As the infra-red spectra of the ethyl and isopropyl esters show an identical wave number pattern of the O-Alk. stretching bond, it may be that this stabilisation of the transition state is sufficient to cancel out variations in bond strengths in the various esters.

leading to the more uniform spread observed of the onset temperatures.

(b) A further point is that for the isopropyl esters a statistical factor comes into play. This allows the carbonyl oxygen atom to interact with any one of six hydrogen atoms, as compared to only three for the primary esters. This doubtless facilitates and accelerates the scission, if the Hurd and Blunck mechanism is assumed.

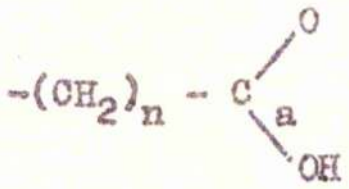
Since these are the only significant structural differences between the primary and secondary esters, it is suggested that the lowering of the onset temperature and the smaller spread of results are due to factor (a), either alone or in conjunction with (b).

16.3. <u>R = Et. n = 1 - 8 and n = 12 B^2 type scission</u>

The ethyl esters of the acids $HO_2C(CH_2)_{\underline{n}}.CO_2H$, ($\underline{n}$ = 1-8 and $\underline{n}$ = 12) were again pyrolysed this time to establish the onset temperature of B^2 scission. The products in every case were acetaldehyde and another aldehyde, the former being detected in the optical cell.

The onset temperatures for B^2 scission were as below:

that on esterification of a series of acids the ratio of C-O bond lengths remains constant, the following figures can be given:-



Acid	Bond length, a
Succinic[106]	1.30
Glutaric[106]	1.30
Adipic[106]	1.38
Pimelic[107]	1.38

The strength of this C-O bond (the breaking bond in B^2 scission) will be directly proportional to its length. These figures suggest an explanation of the stability of the succinate as compared to the adipate and pimelate: but the stabilities of the glutarate and succinate would be expected to be similar, which is not so.

16.4. R = Pr^1 n = 1 - 8 and n = 12 B^2 type scission

The isopropyl esters of the same series of acids were pyrolysed and the onset temperatures obtained given as below. Products of pyrolysis were acetone and the appropriate aldehyde.

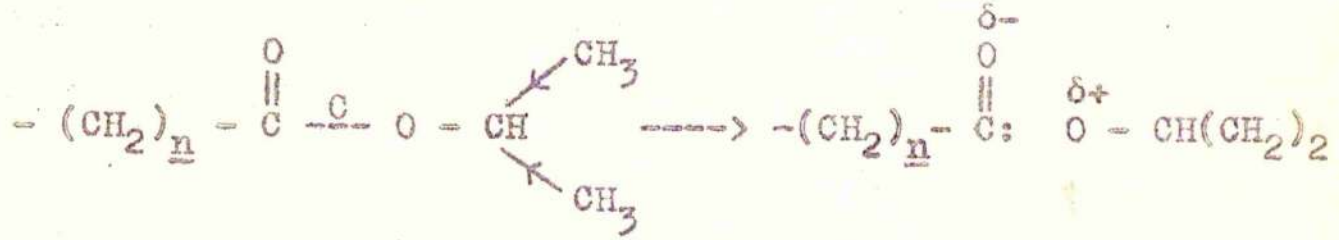
Isopropyl Ester	T($CH_3.CO.CH_3$)
Malonate	205°
Succinate	320°
Glutarate	308°
Adipate	275°
Pimelate	300°
Suberate	297°
Azelate	280°
Sebacate	308°
Tetradecan-1,12-dioate	310°

Isopropyl succinate and adipate were again found to exhibit maxima and minima in the plot of T($CH_3.CO.CH_3$) *vs.* n, just as in A^1 scission of the ethyl esters. The difference in their onset temperatures is again *ca.* 50°.

The latter members of the series all have onset temperatures within the range 280 - 310°, which is only *ca.* 5 - 20° lower than the temperatures recorded for B^2 scission of the ethyl esters. The effect of the extra

methyl group in the alkyl portion of the ester on the two modes of scission, viz. A^1 and B^2, can therefore be compared from a study of the onset temperatures. From the figures quoted for A^1 and B^2 scission of the ethyl and isopropyl esters it can therefore be seen that, as expected, the methyl group exerts a larger influence in A^1 scission where it can exert a stabilising influence on the transition stage of the Hurd and Blunck postulated mechanism, than in the B^2 scission where no stabilisation of a transition stage is possible.

The slight electron repulsion of the methyl group in B^2 scission exerts an influence along the C-O bond C (diagram below) causing a slightly greater electron displacement than for the ethyl esters, thus facilitating ionic breakdown. The scheme suggested is:



Again, no decrease in onset temperature with increase in molecular weight could be detected.

A sample of isopropyl succinate was maintained at 290° for one hour. No breakdown whatsoever was observed. However, on raising the temperature slowly to 318°, breakdown occurred. This result is similar to that

obtained by Norris and Cresswell[91] in the pyrolysis of isobutyl triphenylacetate and tends to confirm the view that the onset temperature has a definite significance.

For the isopropyl esters, B^2 onset temperatures were again lower than the A^1 onset temperatures for the corresponding ethyl esters. It is postulated (p.125) that the six-membered ring transition state is more favoured at higher temperatures, and that, once a suitable temperature has been attained, this reaction proceeds much faster than B^2 scission, which is not so temperature dependent.

16.5. R = Me. n = 1 - 8. B^2 scission.

An attempt to ascertain the onset temperatures of alkyl-oxygen scission (type A°) of the methyl esters was not successful, most of them yielding no detectable olefin up to ca. 470°. However, B^2 scission was noted at temperatures in the range 400-475°, far higher than any of the B^2 onset temperatures previously reported.

Methyl Ester	T(H.CHO)
Malonate	340°
Succinate	475°
Glutarate	452°
Adipate	435°
Pimelate	435°
Suberate	425°
Azelate	405°
Sebacate	408°

There is a general decrease of onset temperature as n increases, in contrast to the ethyl and isopropyl esters. Brown[108] has done considerable work on the pyrolysis of methyl esters of the same series at 500° in a flow-reactor, and has shown that they are very stable at high temperature. His figures (below) indicate the stability of the esters, and also the relatively small amounts of olefin formed by A° scission as compared to other modes of breakdown.

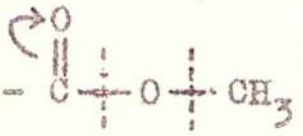
	Decomp.(%)	Res.Time (sec.)	Gaseous pyrolysate		
			Olefin	CO	H_2
Methyl succinate	24	80	8.5	23.0	18.4
" glutarate	23	98	13.8	54.0	6.5
" adipate	30	123	17.6	54.5	6.1
" sebacate	26	185	5.6	36.0	5.2

The stability of the $CO_2.CH_3$ group is also apparent from results with methyl p-toluate which, at high temperatures, yields methyl stilbene -4,4'-dicarboxylate, $CH_3O_2C.C_6H_4.CH = CH.C_6H_4.CO_2.CH_3$ and trioxymethylene. Methyl benzoate is fairly stable at dull red heat[109], no breakdown occurring after 8 hours at 400°.

There is no obvious reason why the B^2 onset temperatures should be so much higher here, and should fail to follow a similar pattern to that of the ethyl and

and isopropyl esters. Possibly a mechanism operates different from that previously suggested; alternatively the volatile aldehyde may be derived from some other source.

Alkyl-oxygen (A°) scission occurs at a far higher temperature than A^1 and A^2 scission, because a six-membered transition state is precluded (see Fig.3): the reaction is therefore probably radical in nature. In this connection it is interesting that acyl-oxygen scission again occurs at a lower temperature. However, if the B^2 reaction does proceed here as previously postulated, formation of products from A° or B^2 scission both require the straight scission of a C-O bond, as follows:-



a = acyl-oxygen scission, B^2

b = alkyl-oxygen scission, A°

The bond energies of bonds a and b must be almost identical (ca. 83 k.cal.). However, because of the proximity-effect of the carbonyl group, bond a will tend to undergo a greater electron shift and hence be more liable to break on pyrolysis, if the reaction is heterolytic. This, in fact, has been found to occur, since B^2 scission occurs at a lower temperature than A° scission.

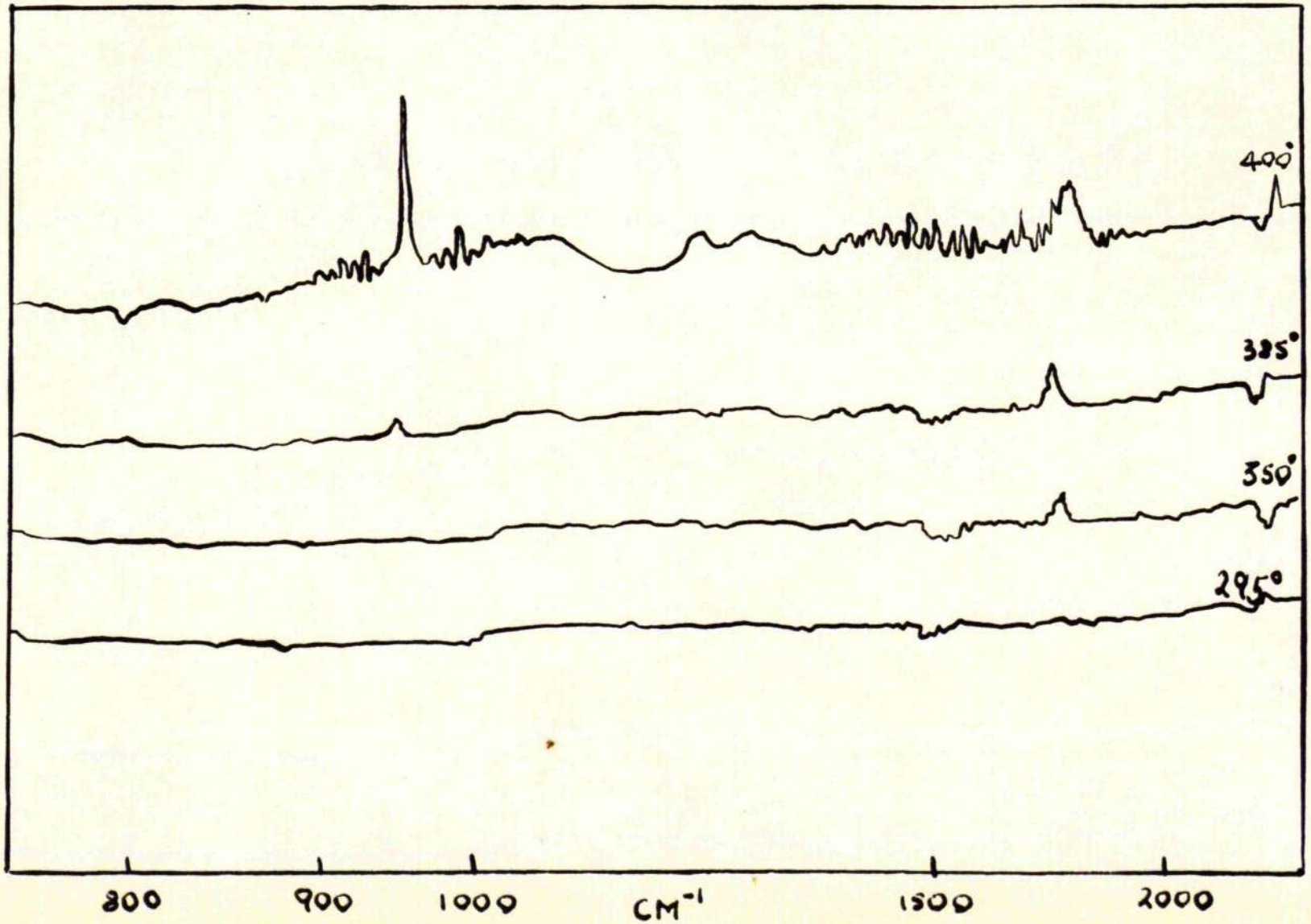
16.6. Onset temperature of methyl malonate

Methyl malonate was pyrolysed in the onset temperature apparatus and formaldehyde was found to be evolved at 340° (confirmed by infra-red spectrum, C = O, 1742 cm.$^{-1}$). The temperature was then raised to 400°; again the only gaseous products were formaldehyde and its breakdown product, carbon monoxide. This would suggested that certain types of breakdown can be isolated by regulation and control of the temperature alone: no trace of any A° breakdown products could be found (gas infra-red spectrometry).

16.7. Onset temperature of ethyl succinate

Ethyl succinate was slowly heated in the apparatus and a gas sample removed for infra-red analysis after the temperature had reached 295° and had been maintained there for several minutes. No trace of any volatile component could be detected. The temperature was then slowly raised to 350° and after a time a sample of gas was again removed for analysis. There was now a sharp but small peak at 1739 cm^{-1}, indicating acetaldehyde C = O, but no trace of any other peak. On further raising the temperature to 385°, a small peak at 950 cm^{-1}, indicating ethylene, became visible, in addition to a slightly larger peak at

FIG 13 ETHYL SUCCINATE: GASEOUS PYROLYSATE I.R.



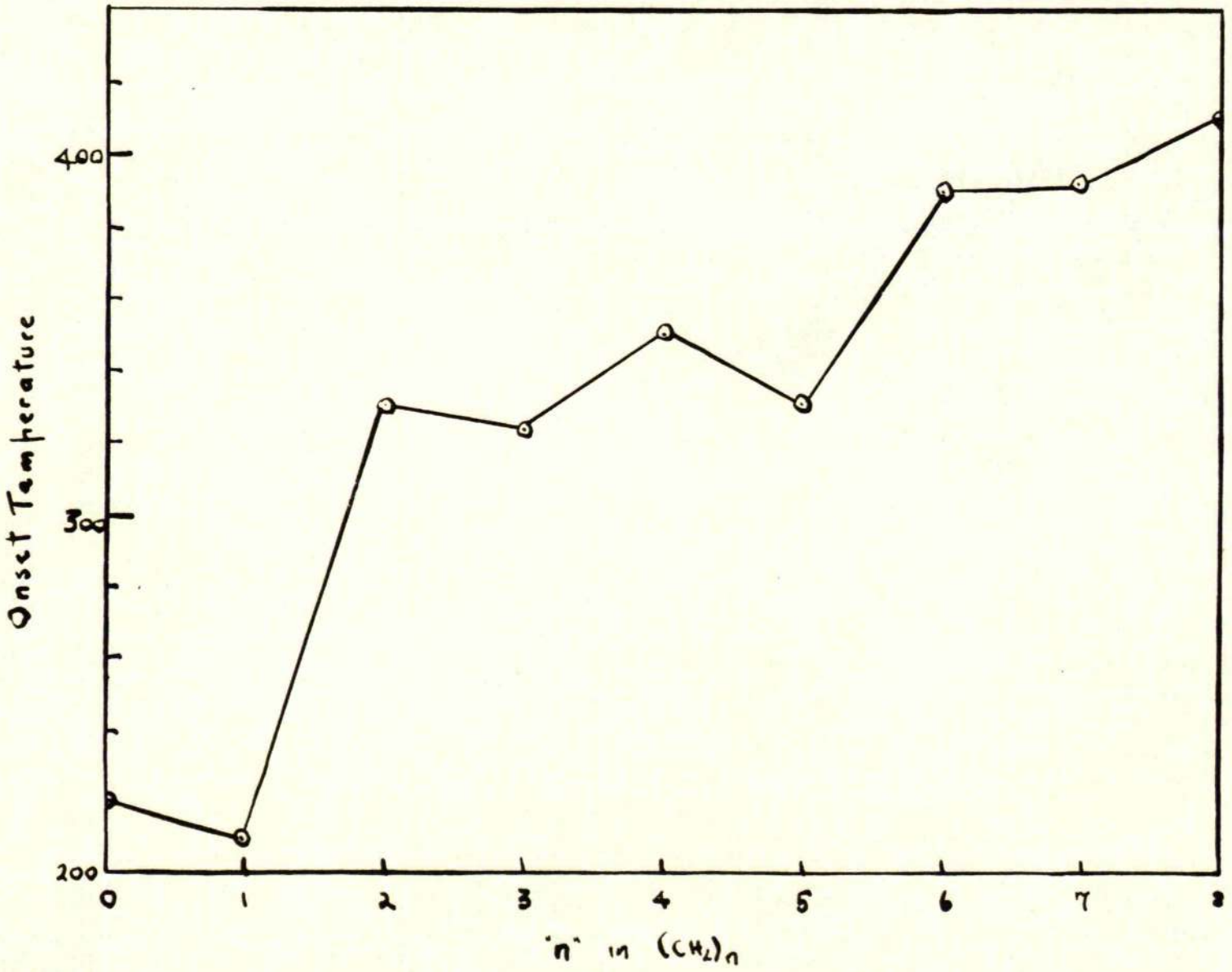


FIG. 14 $T(CO_2)$ OF $HOOC(CH_2)_nCOOH$

1739 cm^{-1}. At 400°, the infra-red spectrum showed a distinctive peak at 1739 cm^{-1}, but the peak at 950 cm^{-1} had greatly increased showing the quick increase in rate once the A^1 scission temperature had passed the onset value of 383°. (Infra-red spectra shown in Fig.13).

16.8. Onset temperature of n-propyl adipate

According to the paper of Smith and Bagley[96], compounds with the same molecular weight should have the same characteristic temperature. If this holds in every case, propyl adipate should show the same onset temperature as ethyl suberate.

The B^2 onset temperature of propyl adipate was found to be 325°, and for ethyl suberate 315°, showing fairly good agreement. However, a gas sample taken from the pyrolysis of the adipate at 355° showed a slight trace of propene as well as propionaldehyde, whereas A^1 scission in the suberate occurs only in the region of 380°. Smith and Bagley's observation therefore does not appear to hold in this case.

16.9. Decarboxylation

The temperature at which the series of acids $(CH_2)_n[CO_2H]_2$ decarboxylated was next studied and the results (below) are in close agreement with those given by Korshak[110] and are shown graphically in Fig.14.

Acid	$T(CO_2)$
Malonic	210°
Succinic	330°
Glutaric	325°
Adipic	350°
Pimelic	330°
Suberic	390°
Azelaic	395°
Sebacic	410°

Alexander et al.[111] investigated a series of long chain normal saturated dicarboxylic acids, and found that their melting points lay on two separate curves, depending whether the acid had an odd or even number of carbon atoms. They then obtained X-ray evidence on the structure of these compounds and concluded that the even and odd numbered members of the acids belonged to two distinct series. This was further shown when the angles between the planes of the carboxyl groups and the carbon chain were worked out by other workers.

Acid	Angle	Acid	Angle
Succinic[106]	9°	Malonic [112]	90°
Adipic [106]	6°	Glutaric[106]	32°
Sebacic [106]	3°	Pimelic [106]	32°

These figures show that the even-numbered acids which all have smaller bond angles between the carboxyl group and the chain than the odd-numbered acids, also have higher onset-temperatures. It is thus likely that the chains in the even-numbered dicarboxylic acids come closer together, and develop stronger intermolecular forces, than do those of the odd-numbered acids. The possibility arises, therefore, that should these intermolecular forces be required to break prior to C^2 scission, the even-numbered members would require more energy and a consequent increase in onset temperature to effect decarboxylation. This is particularly noticeable in the case of malonic acid with a low $T(CO_2)$ and also wide chain separation due to the carboxyl groups being at 90° to the chain.

Here again it is evident that an increase in chain length leads to an increase in onset temperature.

As decarboxylation of saturated esters had not been previously noted, it was decided to measure the C^2 onset-temperature for some of the ethyl esters previously studied.

	$T(CO_2)$
Ethyl malonate	325°
" succinate	390°
" glutarate	360°

For all three esters, the C^2 onset-temperatures agrees very closely with the A^1 onset-temperatures, and are well above the decarboxylation temperatures of the corresponding acids. It seems likely, therefore, that decarboxylation of the ester itself does not occur, but that carbon dioxide is evolved from acid liberated by primary A^1 scission of the ester.

17. Onset Temperatures of Substituted and Unsubstituted Vinyl Benzoates.

Onset-temperatures were established for four separate reactions competing in the pyrolysis of vinyl o-, m-, and p- chlorobenzoates and vinyl benzoate (see p.27).

$X.C_6H_4.CO_2.CH:CH_2$	T(Me.CHO)	$T(CO_2)$	T(CO)	T(CH:CH)
X = H	284°	305°	342°	415°
X = o-Cl	235°	290°	322°	340°
X = m-Cl	255°	295°	330°	384°
X = p-Cl	270°	297°	340°	390°

17.1. Evolution of Acetaldehyde

The observed acetaldehyde is not formed by a primary scission of the esters. T(Me.CHO) is the temperature at which the diester formed from interaction of the original monomer and acid derived from chain-stripping of the polymer (see Section 4.3), breaks down giving the anhydride and acetaldehyde. Ritchie et al.[12] found that vinyl benzoate, refluxed with a molar equivalent of benzoic acid at ca. 280°, yields benzoic anhydride almost quantitatively.

The onset-temperature for evolution of acetaldehyde is not necessarily the temperature at which acid-stripping begins. There is, however, one significant point suggesting some connection between T(Me.CHO) and the temperature of acid-stripping. It has been shown that polymers which allow 5 or 6 membered ring formation of split-off products are unstable. Sensitivity to hydrogen abstraction due to electronegativity of neighbouring atoms or groups or due to resonance stabilisation by neighbouring groups also destabilise a polymer. Thus, from the figures above, it can be seen that the ester without an electronegative Cl atom to cause destabilisation has the highest onset-temperature and that vinyl o-chlorobenzoate with the Cl atom closest to the labile β-hydrogen the lowest breakdown temperature. The m- and p- chloro-compounds occupy intermediate positions. It therefore appears that the onset-temperature depends largely on the stability of the intermediate polymer; and the possibility then arises, bearing in mind the ease with which the acid and ester react at elevated temperatures, that T(Me.CHO) is also the temperature at which acid-stripping sets in.

17.2. Decarboxylation

$T(CO_2)$ has been found to be the temperature of decarboxylation of the ester, not of the corresponding acid. Engler and Low[109] reported that benzoic acid was stable at 390° in a sealed tube, and further onset-temperature studies on the three chlorobenzoic acids have shown that all resist decarboxylation up to 400°.

The small temperature range over which decarboxylation occurs is rather surprising; from the relative quantities of chlorostyrenes and styrene in the pyrolysate from the esters at 500° (see Section 3.4.5.), a greater difference might have been expected between the onset temperatures of the o-isomer, and the other esters. However, $T(CO_2)$ of the o-isomer is the lowest.

T(CO) is probably the decarbonylation temperature of the intermediate labile aroylacetaldehyde which is thought to be formed in the rearrangement of the ester leading to the formation of the acetophenone. Since aldehydes are known to decarbonylate readily, it is possible that the observed onset-temperature, apart from signifying the C^1 of the aroylacetaldehyde, also records the temperature at which this rearrangement occurs.

It is not thought that the carbon monoxide arises from the decarbonylation of acetaldehyde, since it has been

reported by Bone and Smith[113] that acetaldehyde does not break down to methane and carbon monoxide below about 400°.

17.3. Alkenyl-oxygen scission

T(CH ≡ CH)(A^2) has been found to be higher than T(CH_2:CH_2)(A^1) but lower than T(CH_2:CH_2)(A°) for methyl esters. This is probably due, as previously postulated (Section 3.4.4.), to the formation of a six-membered transition stage during the production of the acid and acetylene. This stage is more readily attained by the ethyl esters because of their steric configuration (Fig.1. 2.3.), thus accounting for the lower onset-temperatures. On the other hand, it is sterically impossible for methyl esters, which accounts for their higher onset-temperatures.

The results do not quite agree with those of Smith and Wetzel.[57] Though the relative quantities of acetylene formed in the pyrolysis of the esters at 500° corresponded to their results (i.e. smallest quantity of acetylene from o-ester), the o-isomer had the lowest A^2 onset-temperature. It may be that in the o-isomer, attainment of the transition state is sterically hindered by the bulky chlorine atom, which consequently slows down the formation of acid and acetylene. However, any molecules already in the required steric configuration will undergo alkenyl-oxygen scission, and thus show an onset-temperature lower than that of the other esters. It should be remembered that the temperatures

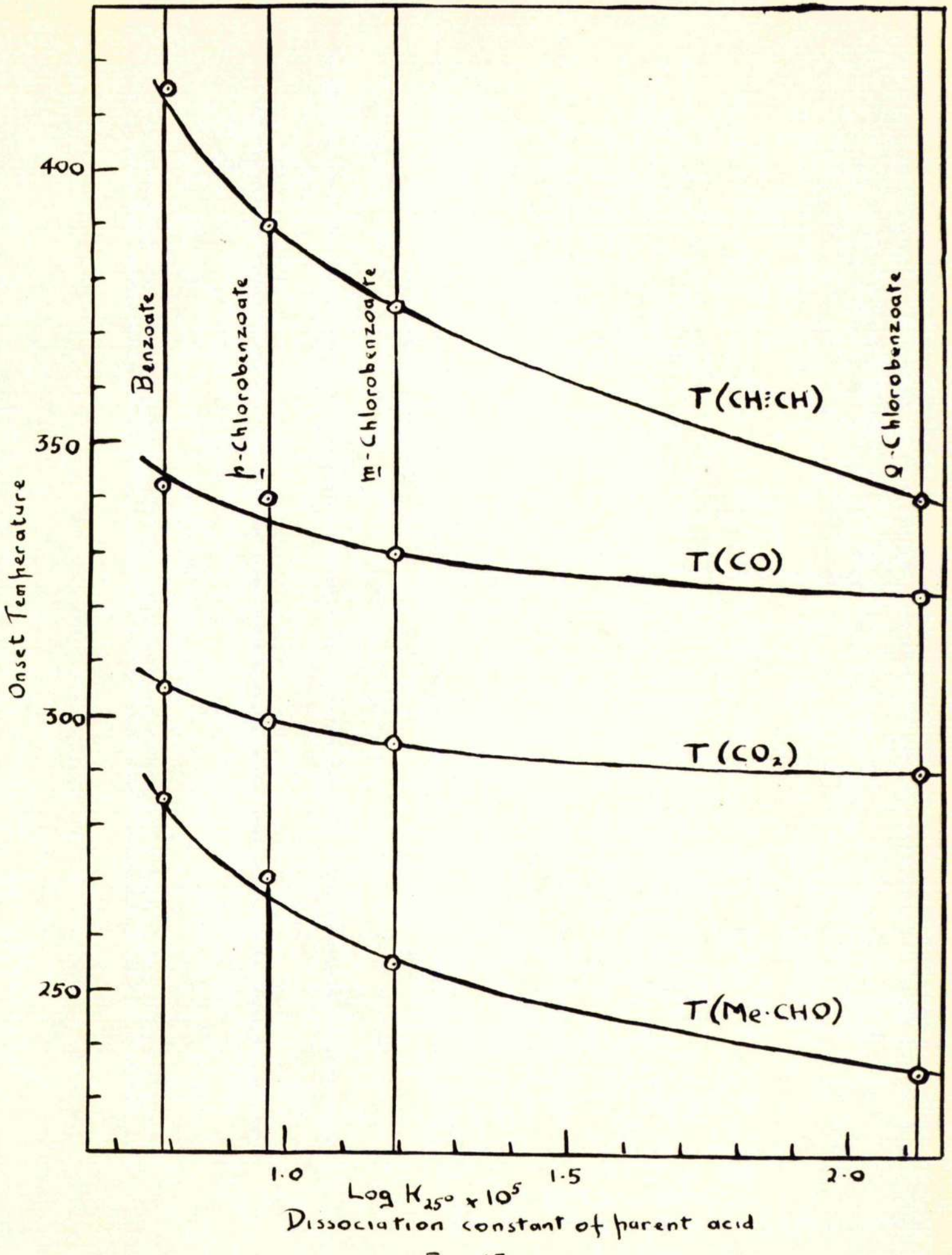

Onset Temperature
400
350
300
250
Benzoate
p-Chlorobenzoate
m-Chlorobenzoate
o-Chlorobenzoate
T(CH:CH)
T(CO)
T(CO₂)
T(Me·CHO)
1·0
1·5
2·0
Log K₂₅° × 10⁵
Dissociation constant of parent acid

FIG. 15

recorded by Smith are those at which pyrolysis occurred most efficiently, and not those at which pyrolysis first occurred.

A plot of onset-temperature against the log of the dissociation constant of the parent acid (Fig.15) suggested by work done by Bailey[105], shows that there is some connection between pKa and onset-temperature though not necessarily direct.

18. Summary

The most striking result from these experiments is that acyl-oxygen scission (B^2) has been shown to occur at a lower temperature than alkyl-oxygen scission (A^1). Till now, it had been assumed that the opposite was the case, as the preponderance of pyrolysate scission products could be explained by an A^1 scission. Behaviour of both ethyl and isopropyl succinate has been shown to be anomalous in various cases and some suggestions have been put forward to account for this.

The relative stability of methyl esters has also been measured and it can be seen that these esters which could most readily form a six-membered transition state also have the lowest onset temperature. This further strengthens the evidence supporting Hurd and Blunck's theory.

APPENDIX

Photopolymerisation with circularly polarised ultraviolet light.

19. Introduction.

Asymmetric influence of circularly polarised light.

Since the beginning of the present century, a few instances of the asymmetric influence of circularly polarised ultraviolet light (C.P.U.V.) have been cited. A few examples are given here.

Van't Hoff[114] in 1894 was the first to suggest that optically active substances might be produced under the asymmetric influence of circularly polarised light, though he did not specifically mention ultraviolet. Results at first proved mainly negative, Cotton[115] and Bredig[116] both quoting figures which showed that C.P.U.V. had no effect on racemic mixtures.

Kuhn and Braun[117] irradiated alcoholic solutions of racemic ethyl α-bromopropionate in quartz vessels with right and left handed C.P.U.V. light. The solution acted on by the right handed light developed a slight dextro-rotation and vice versa. Similar results were recorded by Mitchell[118], who was working with a solution of humuline nitrosite in ethyl butyrate. Kuhn and Knopf[119] exposed the racemic

dimethylamide of α-azidopropionic acid in hexane solution to C.P.U.V. (λ = 3200 - 2800 A°). After 37% decomposition by left handed C.P.U.V., the unchanged fraction of the dimethylamide was isolated and showed a rotation of - 1.049° in a 1 dm. tube. A corresponding experiment with right handed light gave a reading of + 0.78°.

Later, Karagunis and Drikos[120] showed that the addition of chlorine to certain triarylmethyl free radicals, in presence of C.P.U.V., produced optically active products. A total asymmetric synthesis was demonstrated by Davis and Heggie[121], who found that bromine combines with trinitrostilbene in a beam of circularly polarised light (λ=3600 - 4500 A°) to form an optically active (dextrorotatory) product.

Betti and Lucchi[122] claimed to have effected absolute asymmetric synthesis in the gaseous phase. Addition of chlorine to propene and butadiene and of hydrogen chloride to but-2-ene, yielded dextrorotatory products during irradiation with dextrocircularly polarised light and levorotatory products with levocircularly polarised light.

19.1. Stereospecific Polymers

When a monomer of the type $CH_2 = CRR'(R \neq R')$ is polymerised, every second carbon atom in the resulting polymer chain is now asymmetric. Stereoisomerism is thus clearly possible, and is manifested in the three ideal basic types of polymer, designated atactic, syndiotactic, and isotactic.[123]

Isotactic polymers, in which every asymmetric carbon atom has the same steric configuration throughout the chain length, exhibit all the properties associated with polymer crystallinity. Certain catalysts discovered by Natta (e.g. titanium tetrachloride - triisobutylaluminium complex) are claimed to be highly stereoselective, producing isotactic and syndiotactic polymers. The mechanism of this type of heterogeneous catalysis has recently been under discussion, but is not yet exactly known. It has, however, been suggested that the surface of the catalyst itself acts as a mould on which the growing polymer molecule takes a special configuration.[124] Under conditions of total solvation a stereospecific polymerisation has been attributed to small differences in the free energies of the two transition states (each leading to formation of a unit of opposite optical rotation) resulting from interaction between the growing macroradical chain end and the adding monomer molecule.

19.2. Objects of Research

The foregoing examples show that C.P.U.V. light can bring about a certain degree of asymmetric synthesis, or asymmetric decomposition in appropriate systems. No consideration seems hitherto to have been given to the possibility of stereospecific polymerisation of dissymmetrical olefins of the type $CH_2 = CRR'(R \neq R')$ by C.P.U.V. light with production of isotactic polymers (perhaps crystalline). The industrial advantages of such a process, if practicable, cannot be over-rated, as the costs of Natta type catalysts are high. The present work was undertaken to investigate this possibility.

It was thought possible that during bulk polymerisation initiated by C.P.U.V. stereoselective formation of isotactic polymer such as poly(methyl methacrylate) might occur by mechanism analogous to that proposed above for a homogeneous stereospecific polymerisation, i.e. the transition step of each monomer addition stage perhaps being influenced in such a way that preferential formation of one optically isomeric chain might occur. If the first monomer unit of a particular growing polymer chain has a dextro configuration, there is then the possibility that all succeeding monomer units will add on to give a chain in which every monomer unit has the same dextro-rotatory configuration and vice versa.

19.3. Discussion of Results

An optical system was constructed for the production of C.P.U.V. light (see Section 19.4) and a high-vacuum system set up for filling dilatometers with purified monomer.

Methyl methacrylate was selected as a suitable monomer for the present study, since polymerisation data were readily available. A trial experiment was run with methyl methacrylate monomer (no catalyst) contained in a cylindrical dilatometer made of Pyrex glass. During this run, lasting 13 days, polymerisation occurred to the extent of ca. 25%. No crystallinity could be detected by comparison of X-ray diffraction patterns of a film made from the total resultant polymer (completely soluble in boiling heptan - 4 - one; no precipitation after standing for 24 hours) with one of conventional atactic polymer.

It was then decided to attempt to reduce any possible stray interference effects of the circularly polarised light caused by the curvature of the dilatometer wall. Dilatometers used in subsequent runs were therefore constructed with built-in optically flat Pyrex glass discs.

Three runs were carried out in dilatometers thus modified, using

(a) circularly polarised light (no catalyst)

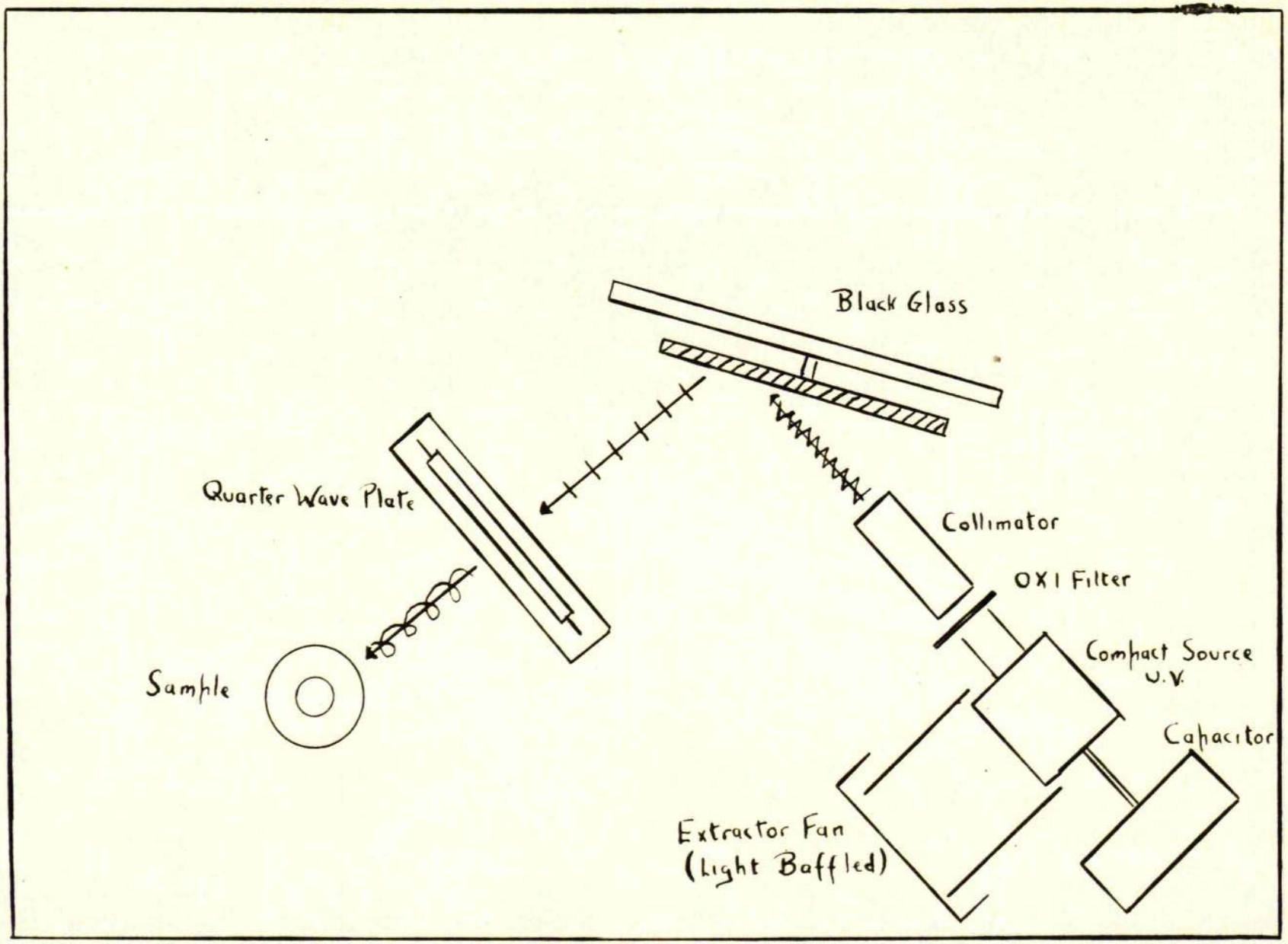

Black Glass
Quarter Wave Plate
Collimator
OX1 Filter
Compact Source U.V.
Capacitor
Sample
Extractor Fan
(Light Baffled)

FIG. 16

(b) circularly polarised light and
azo-bis-isobutyronitrile as catalyst

(c) plane polarised light.

In all of these runs the resultant polymer was found to be totally soluble in heptan - 4 - one which suggested prima facie that no marked degree of crystallinity had been produced.[125] Distinction could not readily be made between isotactic and atactic polymers by means of density measurements (Methyl methacrylate:isotactic d. = 1.19 g./cc., Methyl methacrylate:atactic d. = 1.188 g./cc. Fox[127]). A film of total polymer from each run was made and subjected to X-ray diffraction. No difference in crystallinity could be detected by examination of the diffraction patterns.

It is, therefore, concluded that circularly polarised ultraviolet does not induce isotactic polymerisation of methyl methacrylate, at least under the conditions studied.

19.4. Polymerisation Apparatus

An optical system (see Fig.16) similar to that of Berson and Brown[128] was set up in a light-tight box fitted with two light-baffled apertures through which adjustments could be made to the apparatus. All wall surfaces were painted a matt black to minimise stray reflections. The only illumination was a G.E.C. type ME compact source

mercury arc lamp mounted in a black metal housing fitted with a Chance O X 1 filter to isolate the 3650 A° line. Heat developed by the lamp was removed by means of an extractor fan mounted in a light baffled funnel above the lamp housing. A six inch collimating lens was placed in front of the source at its focal length. The collimated monochromatic beam was plane polarised by reflection from a 6 in. x 9 in. plate of black glass. This plate was mounted in an adjustable clamp and rotated until the reflected beam was plane polarised. Plane polarisation was tested by passing the beam through a Nicol prism on to a fluorescent screen and was indicated by total extinction of the image on the screen when the Nicol prism was rotated to the crossed position. The plane polarised beam was then passed through a specially constructed mica quarter-wave plate (thickness 0.0005°) to achieve circular polarisation. The emergent beam was tested for circular polarisation with a similar quarter-wave plate, a Nicol prism and a fluorescent screen. The filled dilatometer was then placed in this beam with its flat face at 90° to it.

Purification of Monomer

Commercial methyl methacrylate (I.C.I. Ltd.) was freed from inhibitor by shaking with aqueous sodium hydroxide solution followed by washing with distilled water and drying over calcium chloride. The monomer was distilled under reduced pressure and the middle fraction collected for use. Final purification was achieved by distillation on the high vacuum line.

20. X-ray initiated polymerisation

The X-ray polymerisation of solid monomers raises some interesting possibilities. The order in a solid may give preference to a type of addition not normally encountered in the liquid phase. Because of the symmetry of the crystalline lattice and because of the rigidity with which the molecules are held in it, it is possible that orientated and crystalline polymers could result from solid state polymerisation.

In the course of the work described in Part I. of this thesis, vinyl p-chlorobenzoate had been prepared and found to be a white crystalline compound, m.p. 49°. As solid vinyl monomers are uncommon it was therefore decided to polymerise a sample of this ester using X-ray induced initiation.

Several workers have shown the feasibility of inducing polymerisation of monomers by high energy X-ray radiation. One of the first to do so was Mesrobian[129] who polymerised a sample of acrylamide at 22°. Since then many monomers have been polymerised in this way, including methacrylamide, acrylic acid and methacrylic acid (Mesrobian[130]). However, no investigations were carried out into the crystal structure of the resulting polymers until Adler[131] irradiated acrylamide and methacrylamide

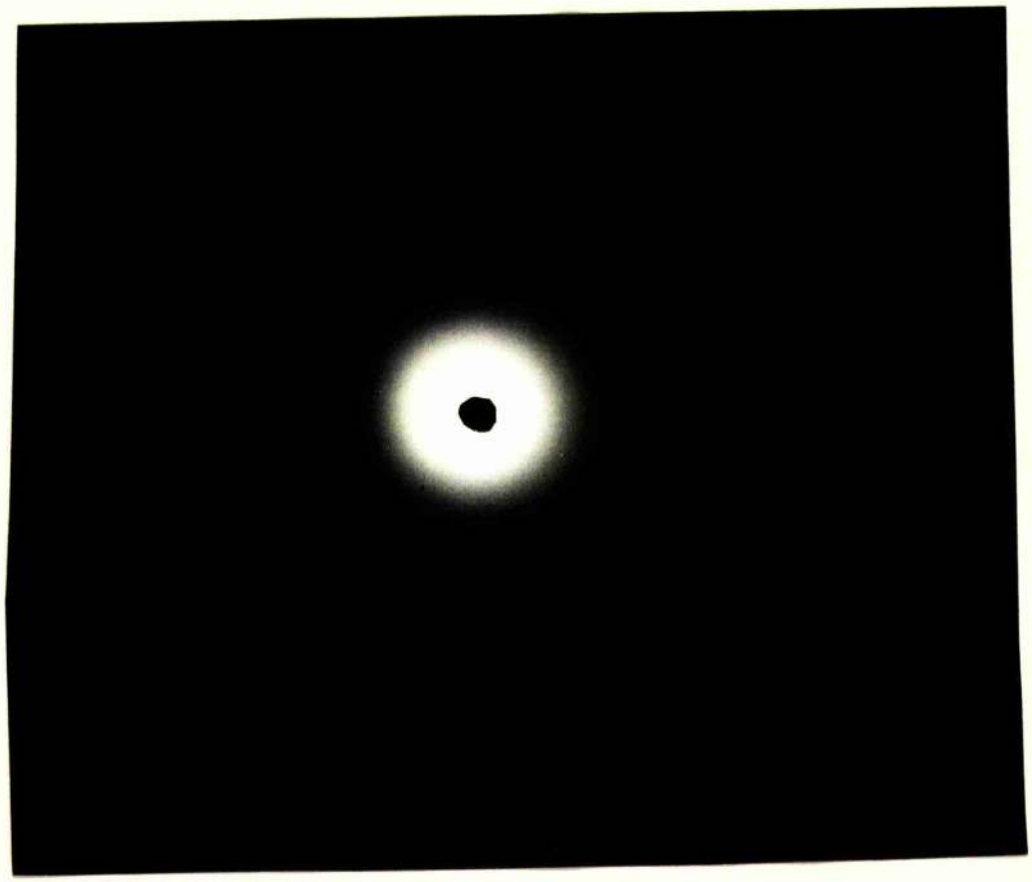


FIG. 17

in a Co^{60} source. From X-ray diffraction patterns he found that the polymers were amorphous.

Accordingly, 5 g. ester was sent to Harwell and the sample placed in a Co^{60} source. The total dose of radiation was 17.5 megerads at a rate of 0.281 megerads/hour.

A film of the resulting polymer was made following washing of the partly polymerised material with methanol. X-ray diffraction patterns of the polymer showed only a broad diffuse ring characteristic of un-orientated and non-crystalline polymers and identical to the diffraction pattern of a sample of catalytically polymerised vinyl p-chlorobenzoate. Diffraction patterns of partially polymerised crystals (Fig.17) showed only diffuse rings with the sharper reflections due to the monomer latice superimposed.

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